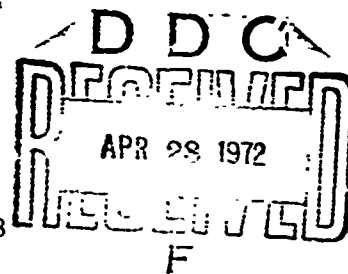# TUNGSTEN FIBER REINFORCED OXIDATION RESISTANT

COLUMBIUM ALLOYS (U)

Final Report

(1 November 1970 to 1 December 1971)

February 1972

By

M. J. Klein and A. G. Metcalfe

Prepared Under Contract N00019-71-C-0158

for

Naval Air Systems Command
Department of the Navy

by

Solar
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The composite developed under this program has good oxidation resistance but is intended to be used in the coated condition with the oxidation resistance serving as a fail-safe protection. The fail-safe life at 2000° F exceeds 100 hours, depending upon the applied load and the volume fraction of filaments. The coated composite performs well under isothermal conditions. For example, a composite with ~24 volume percent filaments has supported a 21 ksi load for almost 700 hours in air at 2100° F without failure. However, the coating tends to crack and allow access of air under cyclic conditions. Work is continuing to further characterize the composite and to extend its service life through improved coating.

14		LINK A		LINK B		LINK C	
KEY WORDS		ROLE	WT	ROLE	WT	ROLE	WT
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Oxidation resistance							
Strength							
Coating							
Columbium alloys							
Tungsten filaments							
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Solar R. P. 6-3589-7

RDR 1693-4

FOREWORD

This is the Final Report for Contract N00019-71-C-0158, Department of the Navy, Naval Air Systems Command. Work covered in this report was completed during the period 1 November 1970 to 1 December 1971. This is an extension of work initiated under a previous contract (N00019-69-C-0137) and reported in detail in the First Annual Report (January 1970) and the Final Report (November 1970). This investigation was performed in the Research Laboratories of Solar, Division of International Harvester Company.

The Principal Investigator for this program is Dr. M. J. Klein, with Dr. A. G. Metcalfe as Technical Director. The Project Engineer for the Department of the Navy is Mr. I. Machlin. Mr. A. R. Stetson and Mr. F. J. Hodnick developed and applied the coatings used in this program. Mr. R. Hutting prepared and assisted in interpretation of metallography, and Mrs. P. J. Lind prepared the program reports.

ABSTRACT

High-strength, oxidation-resistant composites are being developed for use in gas turbine engines at temperatures exceeding 2000° F. In previous work a model system composite consisting of a Cb-40Ti-9Cr-4Al matrix and W-3Re filaments was developed and tested. During the present period, testing of the model system was continued to further characterize this material. In addition, the matrix composition was modified to improve composite ductility. The improved matrix selected for use in the composite is Cb-42Ti-4Cr-4Al-1V.

The composite developed under this program has good oxidation resistance but is intended to be used in the coated condition with the oxidation resistance serving as fail-safe protection. The fail-safe life at 2000°F exceeds 100 hours, depending upon the applied load and the volume fraction of filaments. The coated composite perform well under isothermal conditions. For example, a composite with ~24 volume percent filaments has supported a 2? ksi load for almost 700 hours in air at 2100°F without failure. However, the coating tends to crack and allow access of air under cyclic conditions. Work is continuing to further characterize the composite and to extend its service life through improved coating.

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1

INTRODUCTION

Conventional approaches to develop refractory alloys having both strength and oxidation resistance have been largely unsuccessful because of the difficulty in alloying to achieve both properties in the same alloy. For example, many of the elements which are added to columbium to give the required high strength result in accelerated oxidation rates over those for pure columbium. Similarly, elements that reduce oxidation rates lower the melting point and modulus and, therefore, are undesirable in high-strength alloys. The approach used in this investigation is to combine weak but oxidation-resistant matrices with high-strength filaments to produce a composite with oxidation resistance under loads at temperatures of 2000°F and higher. These operating temperature and strength goals are needed for gas turbine engines, but are beyond the range of nickel- and cobalt-base superalloys which have maximum temperature capabilities of about 1900°F.

Under the initial contract (first annual report, January 1970 and final report, November 1970) various matrices were tested for oxidation resistance, sulfidation resistance, and compatibility with tungsten and sapphire filaments. In addition, various tungsten alloy filaments were tested for strengths and stability at elevated temperatures. A model system composite consisting of 0.010-inch diameter W-3Re filaments in a Cb-40Ti-9Cr-4Al matrix was adopted to assess the feasibility of this approach to alloy development and to identify problem areas that might be inherent in this class of materials.

Although the composite developed has good oxidation resistance, it is intended to be used in the coated condition with the oxidation resistance serving as fail-safe protection. This composite can support significant loads at 2000°F and higher temperatures and has a fail-safe life that will provide protection in the event of coating failure. There are no other available materials that can support comparable loads with fail-safe protection and with significant ductility. However, some composite limitations were also uncovered in the course of this study and it is the objective of this phase of the work to define these limitations and relieve them where possible.

This report, therefore, describes further evaluation of the model system and the results of a study to improve composite properties. This was accomplished primarily by modification of the matrix composition, although some process development

also was found to improve composite properties. A minor amount of work was spent evaluating new composite systems to ensure that all potential composites were evaluated.

Experimental procedures have been described in the first year's report (January 1970) and so they will be reported here only when different techniques are used. For convenience, the model systems consisting of a Cb-40Ti-9Cr-4Al matrix with 0.010-inch diameter W-3Re filaments is designated as J-Alloy/W in this report. A matrix similar to the J-Alloy but possessing somewhat greater ductility will be designated as B-Alloy. The composition of B-Alloy is Cb-42Ti-4Cr-4Al. Most evaluation was performed using composites with 22 to 25 volume percent filaments. For comparison of results from different specimens, some data were normalized to 24 volume percent filaments.

Development of a high-temperature composite of this type requires work on the individual components (matrix, filaments and coatings) followed by work on combinations of these components taken two at a time (e.g., matrix-filament interaction and matrix-coating compatibility) and finally by evaluation of the composite as a whole. The complexity of this development means that an overall assessment of the position at any time is difficult. The present report emphasizes work on matrix optimization to minimize embrittlement problems and has led to selection of an improved matrix for these composites. This work, in turn, has highlighted some deficiencies in the coatings for this system, and work to improve coating performance under cyclic conditions had begun at the end of the contract year. The report concludes with a status report on the properties of the composites based on the optimized matrix but does not include coating improvements recently developed after this contract expired.

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PAST WORK

Tests were conducted to determine longitudinal and off-axis strengths of the model system composite (J-Alloy/24W). The longitudinal strengths are about 170 ksi at room temperature and 50 ksi at 2200°F, and the transverse strengths are about 80 and 6 ksi for the corresponding temperatures. In addition, the strength of the composite is quite stable at elevated temperatures; the longitudinal strength decreases only slightly with increasing holding time up to 100 hours at 2200°F while the strengths for the 45- and 90-degree orientations actually increase.

Oxidation studies of the uncoated composite heat treated at elevated temperatures show that the severity of oxidation attack increases with temperature to about 1600°F, decreases near 1800°F, and increases again at higher temperatures. As a result, the oxidation life of the composite (time to filament attack) in the range 1400 to 1600°F is about the same as the oxidation life near 2000 to 2100°F. The reason for this behavior is not clear, but it was found that this oxidation anomaly occurs only when the composite is oxidized and not when the matrix is oxidized. However, this oxidation behavior should not be a problem since for most applications, the composite will be coated and the fail-safe time should be adequate.

The stress-rupture life of the uncoated J-Alloy/24W in air at 2200°F is about 250 hours for all stresses up to 25 ksi. Although the filaments are protected from oxidation by the matrix, the hardness of the matrix rapidly increases when the composite is heated in air. The rupture life is independent of stress for stresses below 25 ksi because failure is controlled by the kinetics of oxidation rather than by composite creep. If the composite is protected from oxidation failure, the rupture life can be extended to 1000 hours at 2000°F and 22 ksi. In this regard, one of the coated specimens was tested in air for 689 hours at 2100°F and 21 ksi without failure.

Coated and uncoated specimens were subjected to rig tests that closely approach the conditions to which turbine blades are subjected in operational gas turbine engines. The specimens were given fifty 1-hour cycles at 2000°F. Neither the coated nor uncoated composite specimens failed, but the matrix of the uncoated composite showed severe oxidation attack and the coated specimen showed evidence of matrix oxidation through cracks in the coating. The uncoated specimen gained weight during the first 25 cycles as the specimen oxidized and then lost weight during the last 25 cycles due to oxide spalling. In contrast, the coated specimens showed a small uniform weight gain over the period tested.

3

3

NEW COMPOSITE SYSTEMS

3.1 NEW FILAMENTS

In past work under this program a number of 0.10-inch diameter tungsten alloy filaments were evaluated for strength and structural stability. On the basis of these tests, W-3Re (General Electric 3D alloy) was selected for reinforcement of the J-Alloy matrix. However, recent work by Petrasek and Signorelli (NASA-TN-D-5139, 1969) suggest that the alloy W-ThO$_2$ (Westinghouse K-3) may have greater stability than W-3Re and, therefore, may offer advantages over W-3Re for parts subjected to stress for extended periods of time at elevated temperatures. During this period samples of 0.09-inch diameter W-2ThO$_2$ filament, used in the NASA study and supplied by Westinghouse, were evaluated.

Table I summarizes the results of tests to compare the effect of structural stability on tensile strength of W-3Re and W-2ThO$_2$ filaments. The tensile strengths of the filaments were determined at room temperature and 2200°F. The specimens tested at 2200°F were given different pre-test heat treatments to determine the stability of their structures as revealed by changes in tensile strength. Table I shows that the W-3Re and the W-2ThO$_2$ filaments have about the same room-temperature tensile strength. At 2200°F, however, the W-3Re is initially stronger than the W-2ThO$_2$, but as the pre-test heat-treating times are extended, the strength difference between the two filaments decreases. This is shown more clearly in Figure 1.

The results suggest that the W-2ThO$_2$ filaments would be somewhat stronger than W-3Re filaments for long exposures at elevated temperatures. However, their use in the J-Alloy matrix would be contingent upon tests to determine their compatibility with the matrix (i.e., stability of the ThO$_2$ dispersion when the filaments are in the matrix). At this point in the program, there did not appear to be sufficient advantages to warrant substitution of the new filaments for the W-3Re filaments in the model system.

Another potentially viable filament that was considered for use in this program was sapphire single crystal filaments (Tyco). These filaments are attractive because of their resistance to oxidation and low density. The tensile strengths of 0.01-inch diameter sapphire filaments at several elevated temperatures are compared with those for W-3Re in Table II. The sapphire filaments have lower absolute strengths but

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TABLE I

TENSILE STRENGTH OF AS-RECEIVED AND ANNEALED TUNGSTEN ALLOY WIRE

Alloy	Pre-Test Heat Treatment	Number Of Tests	Test Temperature (°F)	Ultimate Tensile Strength (ksi)
W-2ThO$_2$ (Westinghouse K-3)	None	3	Room	390.0
	None	3	2200	136.8
	1 Hour at 2200°F	1	2200	133.6
	10 Hours at 2200°F	1	2200	116.4
	100 Hours at 2200°F	3	2200	117.0
W-3%Re (G.E. 3D Alloy)	None	4	Room	399.4
	None	4	2200	165.5
	1 Hour at 2200°F	2	2200	142.6
	10 Hours at 2200°F	2	2200	125.3
	100 Hours at 2200°F	2	2200	109.2

greater specific strengths at 2000 and 2200°F than the W-3Re filaments. On this basis, sapphire is an attractive material for matrix reinforcement, However, as will be shown in Section 3.2, there are other serious problems involved in using these filaments in composites.

3.2 NEW COMPOSITES

The Fe-Cr-Al/Al$_2$O$_3$ composite system is believed to have excellent potential as a composite for use at high temperatures in an oxidizing environment. Both matrix and filaments have high oxidation resistance, and the filaments yield high specific strengths at elevated temperatures (Table II). In past work, it was shown that the sapphire filaments are compatible with Fe-25Cr-4Al-0.5Ta-0.1Y matrix. During this period, this composite system was studied further to determine its fabricability.
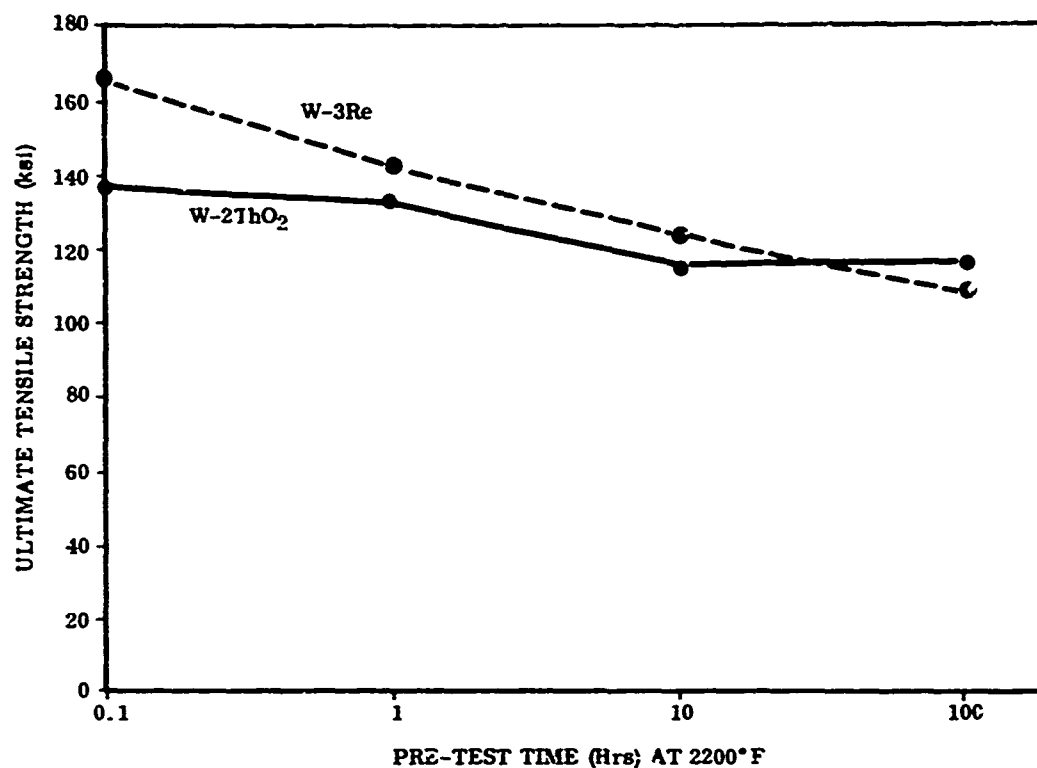
FIGURE 1. EFFECT OF PRE-TEST HEAT TREATMENT AT 2200°F ON
STRENGTH OF W-3Re AND W-2ThO$_2$ AT 2200°F

TABLE II

SPECIFIC STRENGTH VERSUS ABSOLUTE STRENGTH OF Al$_2$C$_3$ AND
W3Re FILAMENTS AT ELEVATED TEMPERATURES

Temperature (°F)	Strength (psi x 10^{-3})		Specific Strength (in. x 10^{-3})	
	Al$_2$O$_3$	W-3Re	Al$_2$O$_3$	W-3Re
1800	76.4	–	–	–
2000	67.5	204	478	293
2200	51.0	165	361	237

Small composite specimens were diffusion bonded using a variety of temperatures and pressures. The sapphire filaments were extracted by dissolving the matrix to determine the amount of filament fracture during bonding. Broken filaments were found in all of the composite specimens where intimate filament-matrix contact had taken place, but there was no evidence of a filament-matrix interaction revealed by metallographic examination. These results suggest that the brittleness of the presently available sapphire filaments will severely limit their use in practical composite systems.

Another composite combination that has potential for use at elevated temperatures is the Fe-Cr-Al/W system. The Fe-Cr-Al matrix is resistant to oxidation and does not become embrittled when exposed to the atmosphere at elevated temperatures. However, past work has shown that the Fe-Cr-Al matrix is not compatible with the W-3Re filaments used in this study, but the filaments are compatible with chromium. Therefore, tungsten filaments were coated with various thicknesses of chromium and then the filaments were diffusion bonded in the Fe-Cr-Al matrix (Fe-25Cr-4Al-0.5Ta-0.1Y). This composite was heated at 2200°F for 100 hours to determine the compatibility afforded by the chromium plating. As shown in Figure 2, this system does not appear to be sufficiently compatible to yield a viable composite.
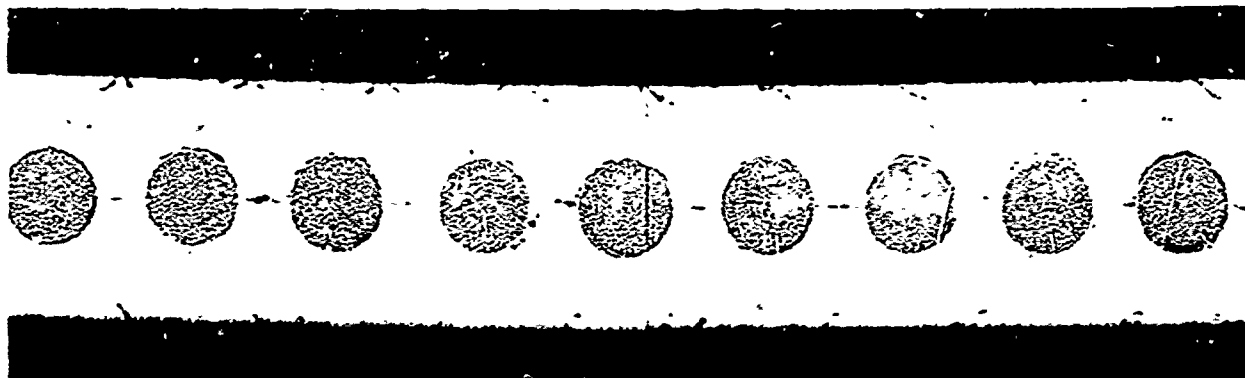
A. As-Bonded
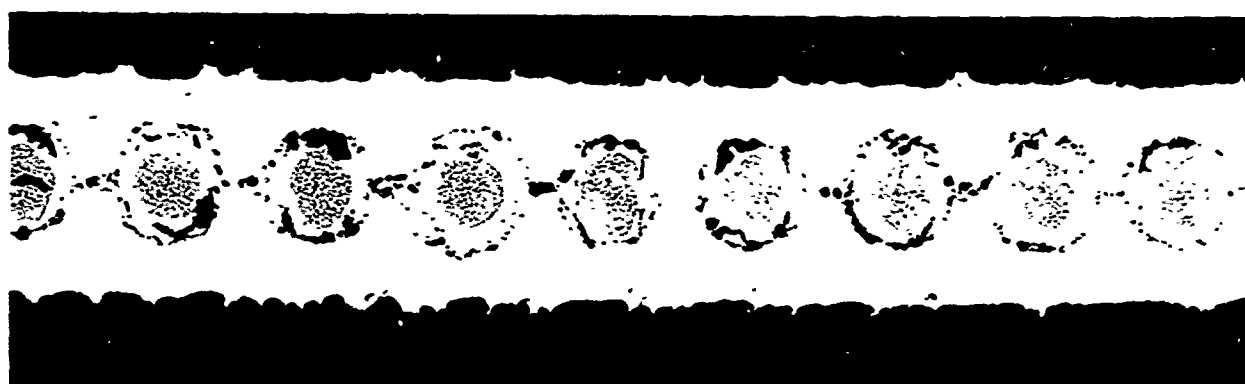
B. After 100 Hours at 2200°F

Magnification: 50X

FIGURE 2. CHROMIUM PLATED TUNGSTEN FILAMENTS IN Fe-Cr-Al MATRIX

4

FURTHER EVALUATION OF MODEL SYSTEMS (J-ALLOY/W)

The model system, J-Alloy/W, was selected early in the program to assess the feasibility of developing a strong oxidation-resistant alloy by combining strong filaments with an oxidation-resistant matrix. The J-Alloy (Cb-40Ti-9Cr-4Al) did not necessarily represent the optimum combination of properties desired for the matrix. However, its early selection for use in the model system did permit rapid identification of problem areas that would require matrix modification to develop a viable composite.

In this section, the results of additional evaluation of the J-Alloy/W composite are presented. The properties studied in this phase of the program are dependent, to a large extent, upon the properties of the matrix. The results of some of these tests provided a basis for advanced matrix development, which is discussed in Section 5.

4.1 PROCESS DEVELOPMENT

The effect of two processing parameters on composites properties were studied. After the composite was fabricated and heat treated for a short time, it was rebonded to reduce Kirkendall porosity upon subsequent heat treatment. The workability of the composite was also studied by cold rolling to large reductions in area and examining the cold rolled structure.

4.1.1 Rebonding

The structure of the J-Alloy/24W composite is characterized by porosity in the matrix after extended exposures at elevated temperatures. This porosity, which is most extensive in the matrix between the filaments, is believed to result from unequal filament-matrix interdiffusion (Kirkendall porosity). Matrix porosity is probably not very detrimental to longitudinal composite strength at elevated temperatures since this is largely determined by filament strength. However, matrix porosity may degrade the transverse strength if it reduces the cross section that is effective in sustaining the applied load. As shown in Figure 3, gross porosity has formed in a stress rupture specimen after about 700 hours at 2100°F. However, analysis of other data indicates that porosity will not be severe and will not be evident metallographically in less than 1000 hours at 1800°F.

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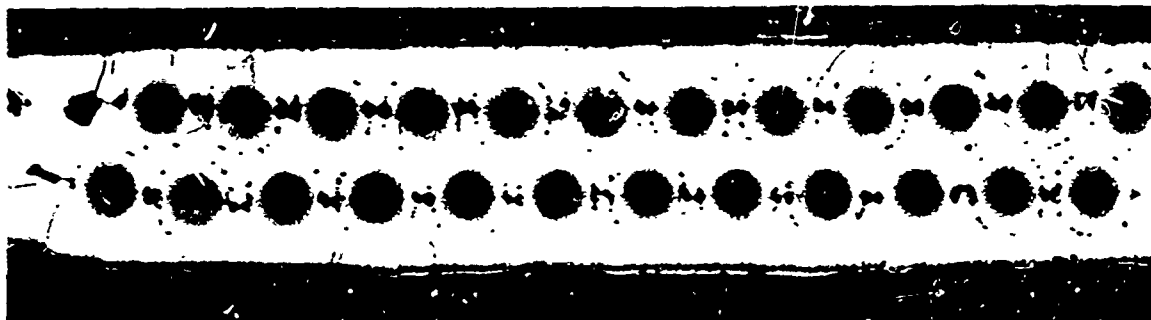
FIGURE 3. POROSITY IN COATED J-ALLOY/24W AFTER STRESS
RUPTURE TEST IN AIR FOR 689 HOURS AT 2100°F
AND 21 KSI APPLIED STRESS

In order to reduce porosity in the composite, a technique was develope[1] whereby heat treatments were interrupted to rebond the composite. The rebonding should serve to eliminate pores that may be present at the filament-matrix interface after the initial bond and may also be preferred sites for vacancy precipitation during the initial heat treatment. In addition, the concentration gradient in the rebonded specimens would be much reduced because of interdiffusion during the initial heat treatment. The reduced concentration gradient in the rebonded specimens would decrease the tendency for Kirkendall porosity formation during subsequent heat treatments of the rebonded specimens. In Figure 4, the structure of the continuously heat-treated specimens are compared with the structure of specimens whose heat treatments were interrupted for rebonding. The results show that the rebonding technique is very effective in reducing Kirkendall porosity in the J-Alloy/24W composite. However, as shown in this figure, cracks were detected in the composite heated for 30 hours at 2400°F, indicating that the matrix may be embrittled by filament-matrix interdiffusion. This problem will be considered later in Section 4.

4.1.2 Cold Rolling

Although only a limited amount of composite working has been performed, the general workability of the system has been demonstrated. The composite · as cold rolled to 85 percent reduction in thickness without any intermediate heat treatments. Cross sections of the rolled structures are shown in Figure 5. There is no evidence of filament or matrix cracking resulting from rolling. The ductility of this composite is in contrast with the brittle behavior of metal matrix composites with non-metallic filaments. Filament breakage is no problem in this system, whereas it is a major problem in composite systems with non-metallic filaments.
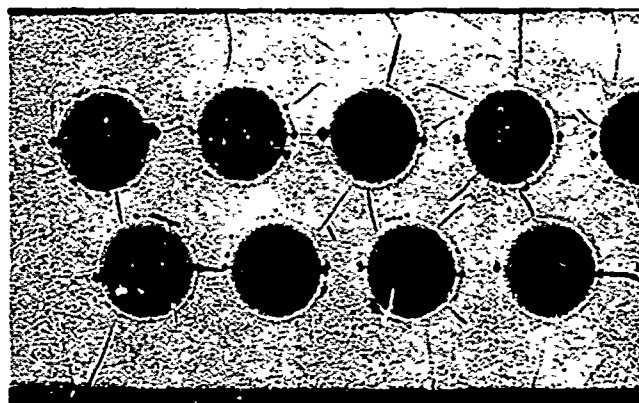
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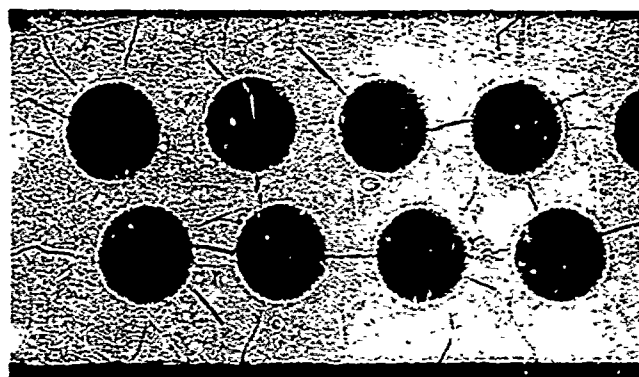
1 Hour at 2400°F, Rebond Plus
9 Hours at 2400°F
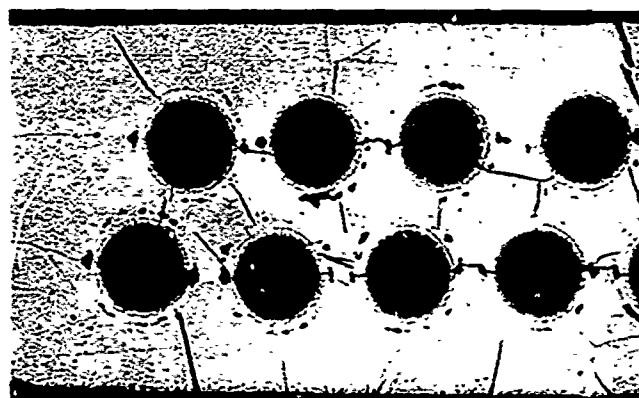
30 Hours at 2400°F
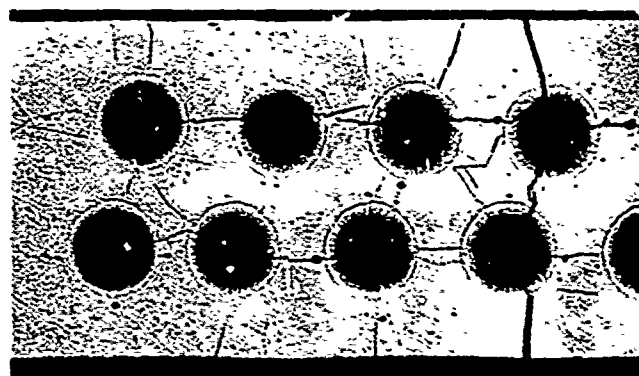
1 Hour at 2400°F, Rebond Plus
29 Hours at 2400°F

Magnification: 50X

FIGURE 4.   EFFECT OF REBONDING ON POROSITY IN J-ALLOY/24W

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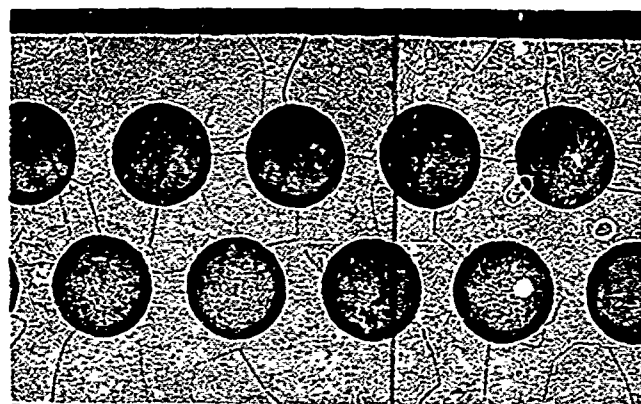
As Fabricated

72 Percent Reduction
in Thickness

85 Percent Reduction
in Thickness
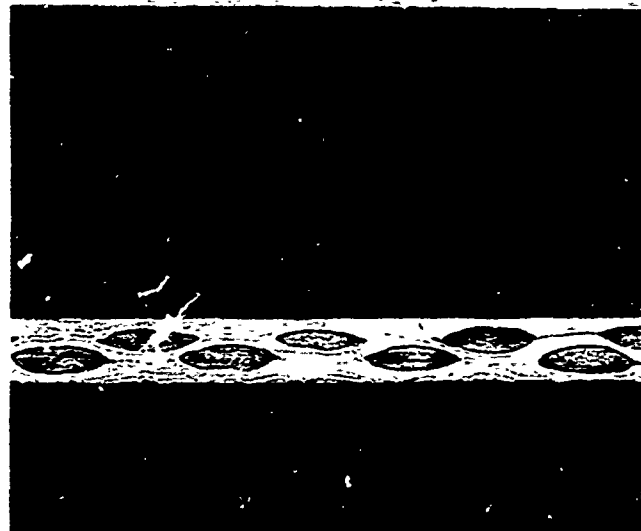
Magnification: 50X

FIGURE 5. J-ALLOY/W COMPOSITE COLD ROLLED TO 72 AND 85 PERCENT
REDUCTION IN THICKNESS

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4.2 TRANSVERSE STRENGTH OF J-ALLOY/W AT ELEVATED TEMPERATURES

In this section the effects of processing variables on the transverse strength of J-Alloy/W at elevated temperatures are described. The elevated-temperature transverse strength is an important property of high-temperature composites since it indicates the minimum off-axis strength at temperatures of use. The processing variables studied were cold rolling, heat treatments, and rebonding of the composite.

4.2.1 Effect of Cold Rolling

After fabrication, strips of J-Alloy/W (approximately 25 volume percent tungsten) composite were cold rolled various amounts ranging from 25 to 85 percent reduction in thickness. The transverse strength of the rolled composite strips was then determined at 2200°F for comparison with the transverse strength of the as-fabricated composite. The results of these tests are listed in Table III. Cold rolling does not degrade the elevated-temperature transverse strength. Only the specimen rolled to 85 percent reduction in thickness has a significantly lower transverse strength than the as-fabricated composite, and as will be shown later, this specimen may have failed at a lower stress level because of filament misalignment. The last specimen listed in Table III was given a 1-hour heat treatment at 2400°F and rebonded (2250°F/ 7.5 ksi/60 seconds) after being rolled to 74 percent reduction in thickness. The treatment after cold rolling has increased the transverse strength to 7.6 ksi, well above

TABLE III

EFFECT OF COLD ROLLING ON TRANSVERSE TENSILE STRENGTH OF J-ALLOY/W AT 2200°F

Cold Rolling Of Composite				Transverse Strength At 2200°F (ksi)
Initial Thickness (mils)	Final Thickness (mils)	Reduction In Thickness (%)	Treatment After Cold Rolling	
40	40.0	0	None	5.7
40	30.0	25	None	5.8
40	13.0	67	None	6.5
40	10.8	73	None	5.5
40	6.0	85	None	4.8
40	10.4	74	1 Hour 2400°F and Rebond	7.6

the transverse strength of the as-bonded composite. These results show that this composite system has high ductility and can sustain a large amount of deformation without degradation of elevated-temperature transverse strength. Matrix or filament cracking as a result of deformation would degrade the strength of the composite and would be evident upon metallographic examination of the composite. Figures 6, 7 and 8 show the structure of the composite after transverse testing. The mechanism of transverse failure is unchanged by cold rolling. Figure 6 presents the structure of an as-fabricated specimen and a cold-rolled specimen after transverse testing at 2200°F. Failure in both specimens is at the filament-matrix interface. Figure 7 shows the structure of the transverse specimens reduced 85 percent in thickness before transverse testing at 2200°F. Failure in this specimen has occurred where the filaments are improperly spaced. The filament spacing at the region of failure leaves very little matrix to support the transverse load, and this is believed to be the reason for the somewhat reduced transverse strength of this specimen. The change in failure mode induced by heat treating and rebonding after cold rolling is shown in Figure 8. Here, transverse failure is through the filaments rather than at the interface. The transverse strength is increased because the interface has been strengthened.

4.2.2 Effect of Other Processing Variables on Transverse Strength of J-Alloy at 2200°F

The effect of other single processing variables and their combined effects on transverse strength of J-Alloy/W are listed in Table IV. Heat treatments at 2400°F after fabrication increase the transverse strength to 6.5-6.8 ksi (No. 1, Table IV). Heat treatments combined with rebonding increase the strength to 7.7 ksi (No. 2, Table IV), the highest transverse strength attained in this series of tests. As discussed above, cold rolling alone (No. 3) does not appear to have a detrimental effect on transverse strength, but cold rolling followed by heat treatment yields a higher transverse strength than heat treatment followed by cold rolling (No. 4). When the cold rolling and heat treating are followed by rebonding, the strength is increased still further (No. 5). In summation, the following processing treatments increase the transverse strength: heat treating; heat treating and rebonding; cold rolling and heat treating. Cold rolling alone does not reduce the transverse strength if filaments are properly aligned, but cold rolling after heat treatment is detrimental to transverse strength.

4.3 OXIDATION CHARACTERISTICS OF J-ALLOY

Additional oxidation tests of J-Alloy were performed to further define the oxidation resistance of this alloy and to form a solid base to evaluate the oxidation resistance of other potential matrix alloys. The latter will be discussed in detail in Section 5, Advanced Matrix Development.
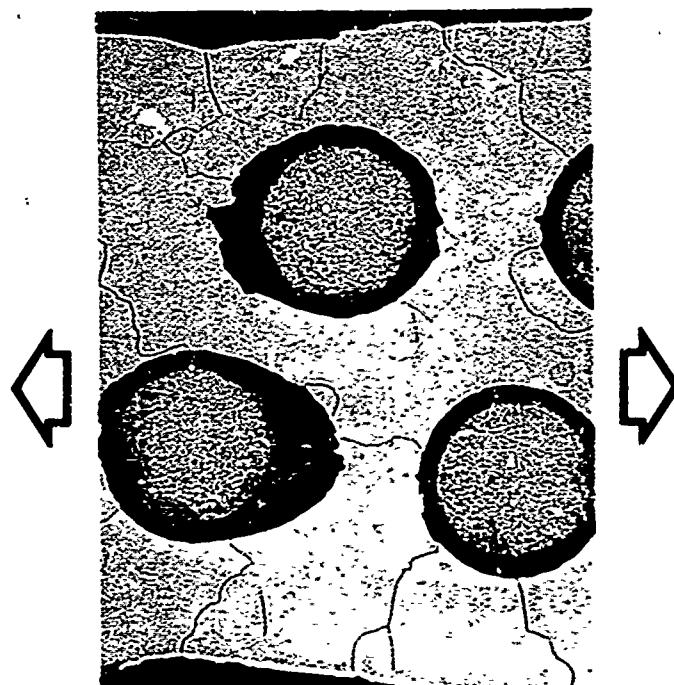
A. As-fabricated and tested (5.7 ksi)
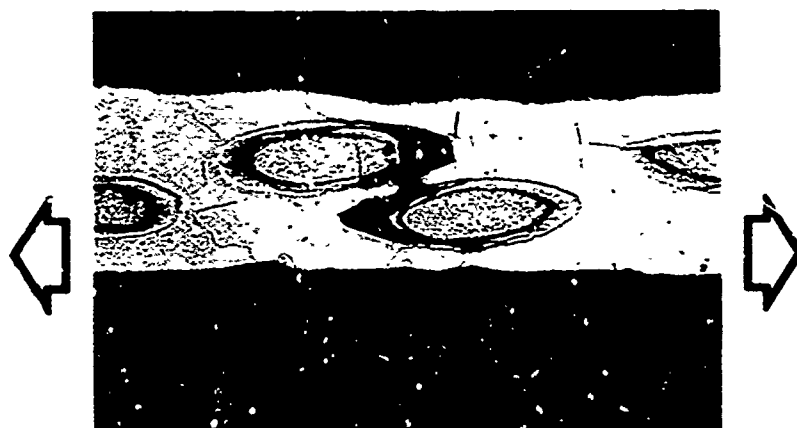
B. Reduced 73 percent in thickness and tested (5.5 ksi)

Magnification: 100X

FIGURE 6. TRANSVERSE TENSILE SPECIMENS OF J-ALLOY/W
TESTED AT 2200°F
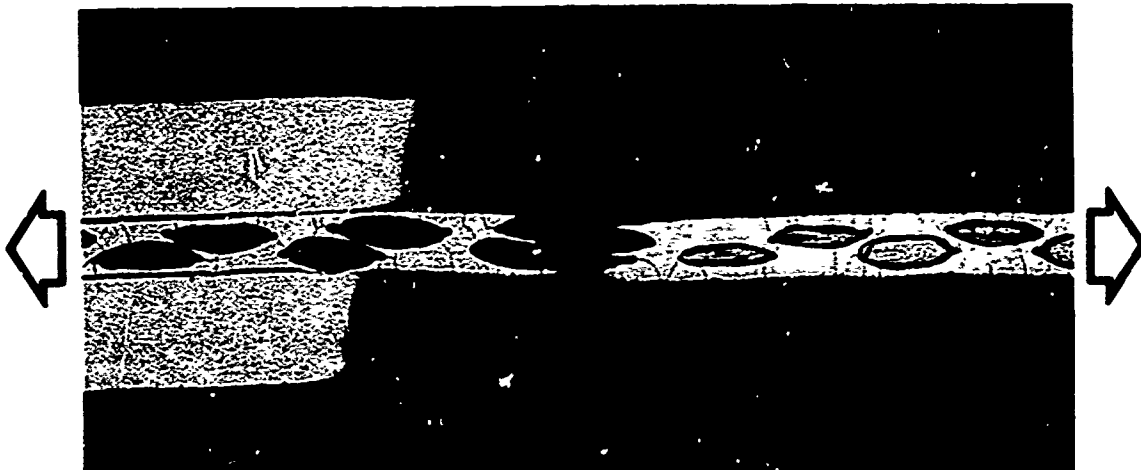
FIGURE 7. TRANSVERSE TENSILE SPECIMEN OF J-ALLOY/W TESTED AT
2200°F AFTER 85 PERCENT REDUCTION IN THICKNESS
(4.8 KSI) (Magnification: 50X)
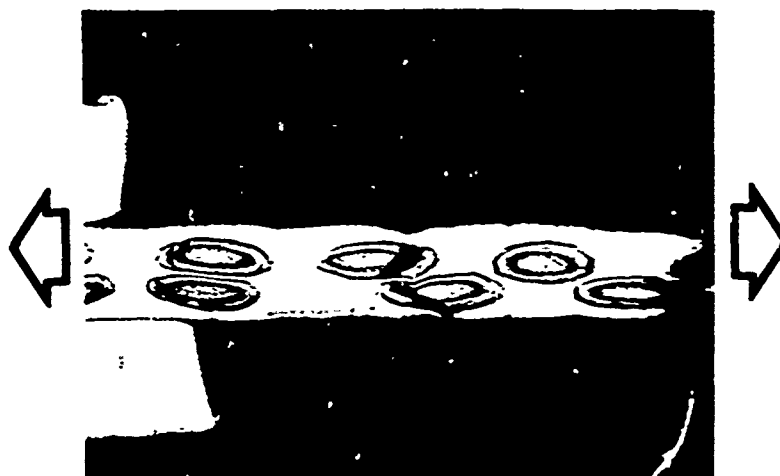
Magnification: 50X

FIGURE 8. TRANSVERSE TENSILE SPECIMEN OF J-ALLOY/W
TESTED AT 2200°F; Pre-test Treatment – 74 Percent
Reduction In Thickness, 1 Hour at 2400°F and Rebond
(7.6 ksi)

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TABLE IV

EFFECT OF PROCESSING VARIABLES ON TRANSVERSE STRENGTH
OF J-ALLOY/W AT 2200°F (~25% REINFORCEMENT)

Pre-Test Treatment	Transverse Tensile Strength At 2200°F (ksi)
1. Effect of Heat Treatment	
As-fabricated	5.7
2400°F - 1 hour	6.5
2400°F - 10 hours	6.8
2. Effect of Heat Treatment and Rebonding	
2400°F - 1 hour plus rebond	6.9
2400°F - 1 hour, rebond plus 9 hours at 2400°F	7.7
3. Effect of Rolling	
25 percent reduction in thickness	5.8
67 percent reduction in thickness	6.5
73 percent reduction in thickness	5.5
85 percent reduction in thickness	4.8
4. Effect of Rolling and Heat Treatment	
25 percent reduction plus 1 hour at 2400°F	6.9
1 hour at 2400°F plus 25 percent reduction	5.0
5. Effect of Rolling, Heat Treatment and Rebonding	
74 percent reduction plus 1 hour at 2400°F plus rebond	7.6

4.3.1 Effect of Specimen Thickness

The oxidation rate of various specimens of J-Alloy at 1600 and 2000°F are compared in Figure 9. The dashed lines in this figure show the oxidation rate of J-Alloy/24W composite determined previously. The multi-layered specimens are 0.012-inch foils of J-Alloy rolled from arc-melted ingots and diffusion bonded together without tungsten filaments. The three-layered specimen is similar to the composite in that both contain three layers of foil ·˙ .fusion bonded together. The results show that the oxidation kinetics, as revealed by the specimen weight gain, are a function of the number of layers of J-Alloy in the specimen. For example, the weight gain of the one-layer specimen after ~100 hours at 1600°F is less than half that of the six-layer specimen.

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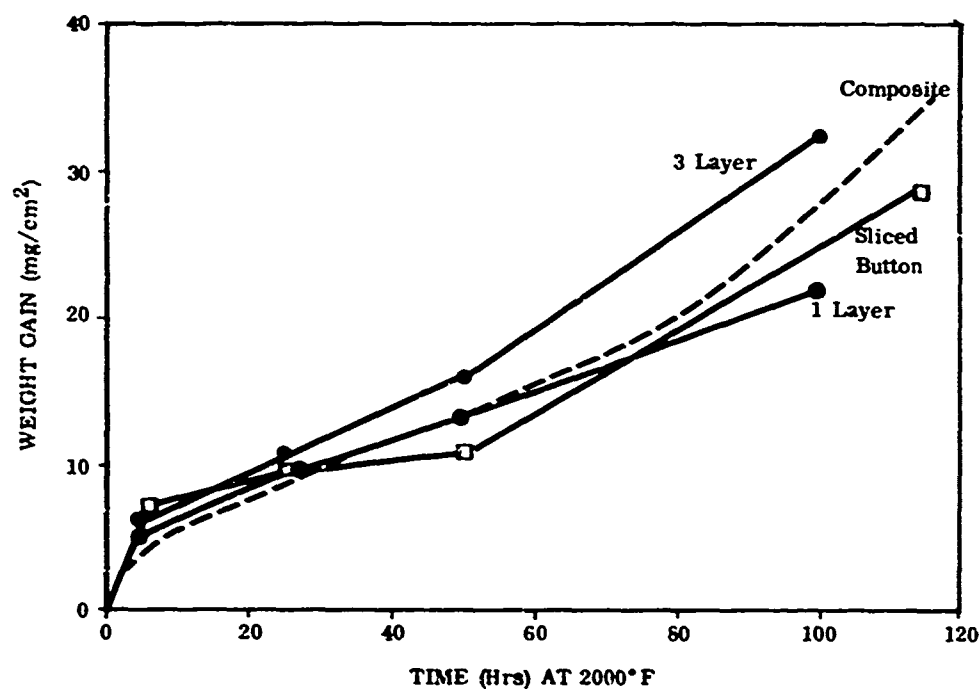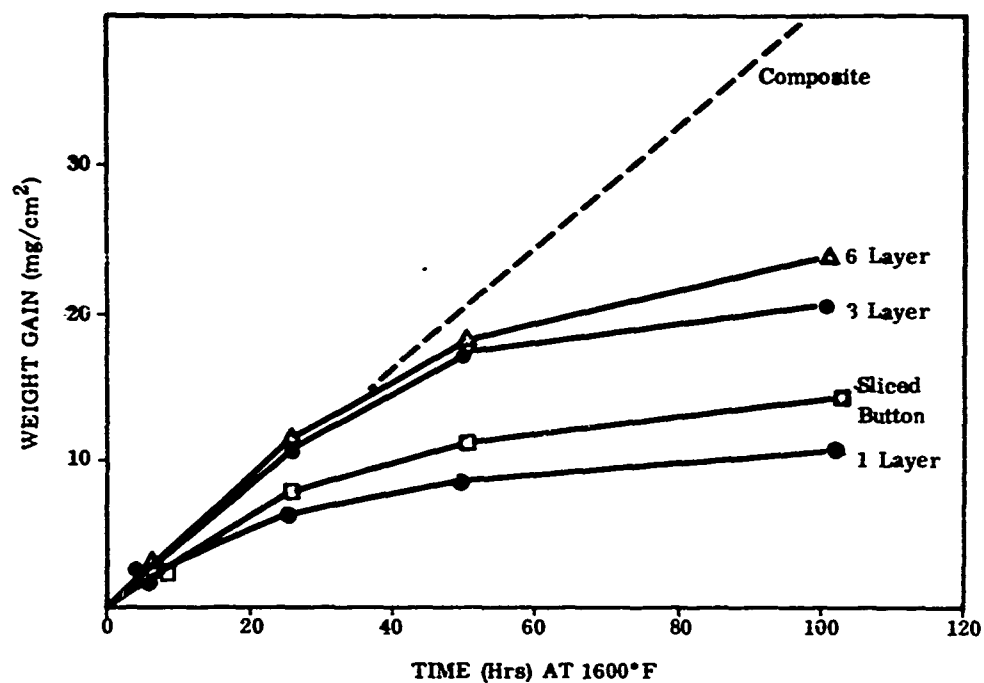
FIGURE 9. OXIDATION OF DIFFERENT TYPES OF SPECIMENS OF J-ALLOY
AT 1600 AND 2000°F; The Multi-Layer Specimens are 0.012 Inch
Sheet Diffusion Bonded Together and the Sliced Buttons are 0.10
Inch Coupons Sliced from Arc Melted Buttons

The data for the sliced buttons shown in Figure 9 are for 0.10-inch thick coupons sliced from arc-melted buttons. At 1600°F the oxidation rate for the sliced button is slightly greater than that for the one-layer specimen, and at 2000°F their oxidation rates are about the same. In this regard, the oxidation rates for the various types of specimens are closer at 2000°F than at 1600°F.

The oxidation rate of the composite at 1600°F is about the same as the oxidation rates for the three- and six-layer specimens for times up to 50 hours. For greater oxidation times at this temperature, the composite oxidizes at a greater rate than any of the matrix specimens. However, at 2000°F the oxidation rates for the composite and the matrix specimens are about the same.

The structure of the J-Alloy specimens after the 100-hour oxidation at 1600°F are shown in Figure 10. The scale thickness is greatest for the six-layer specimen and least for the one-layer specimen and the sliced button. The scale thickness is thus proportional to the weight gain at 1600°F shown in Figure 9. However, despite the low weight gain and scale buildup, the one-layer specimen has an oxidation induced second-phase structure throughout the matrix, whereas the thicker specimens have central regions free of this oxide phase.

These results show that comparison of the oxidation of candidate alloys with the oxidation of J-Alloy should be made using specimens with the same shape, thickness, and metallurgical history. After the initial screening, final comparisons should be made using composite specimens.

4.3.2 Pre-Oxidation Effects

Composite specimens were oxidized in air at 1200°F for approximately 100 hours and then the specimens were oxidized again at higher temperatures. This 1200°F treatment produced negligible weight gain. The structure of the pre-oxidized specimen and a specimen that was not pre-oxidized are compared in Figure 11 after both specimens had been oxidized at 1600°F for about 160 hours. It is evident that the pre-oxidized specimen is much more resistant to 1600°F oxidation attack than the specimen that was not pre-oxidized.

The improved 1600°F oxidation resistance of the pre-oxidized specimen is also evident from a comparison of weight gain-time profiles. As shown in Figure 12, the total weight gain for the pre-oxidized specimen (including the weight gain at 1200°F) is about one-fourth that of the specimen oxidized directly at 1600°F. However, at higher temperatures the benefit of the 1200°F pre-oxidation treatment seems to be largely lost (Fig. 13).
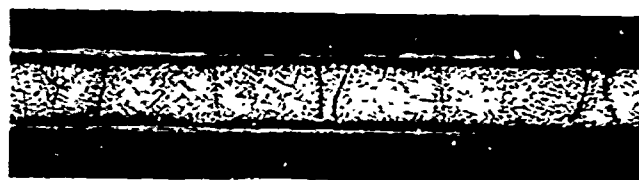
A. One Layer
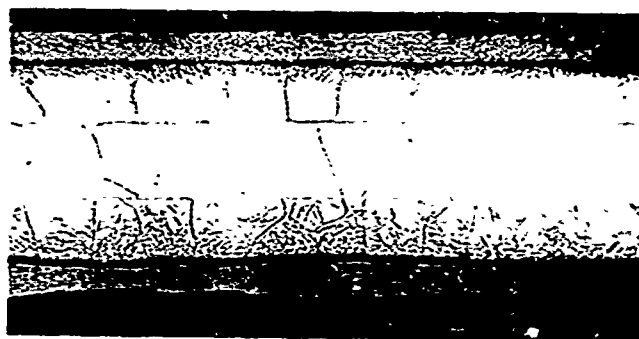
B. Three Layers
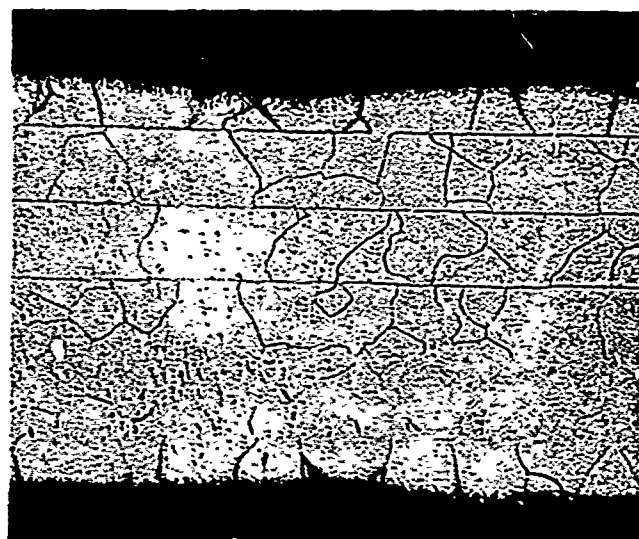
C. Six Layers

D. Sliced Button

Magnification: 35X

FIGURE 10. STRUCTURE OF ONE-, THREE- AND SIX-LAYER SPECIMENS AND
ARC MELTED BUTTON OF J-ALLOY AFTER ~100 HOURS AT 1600°F
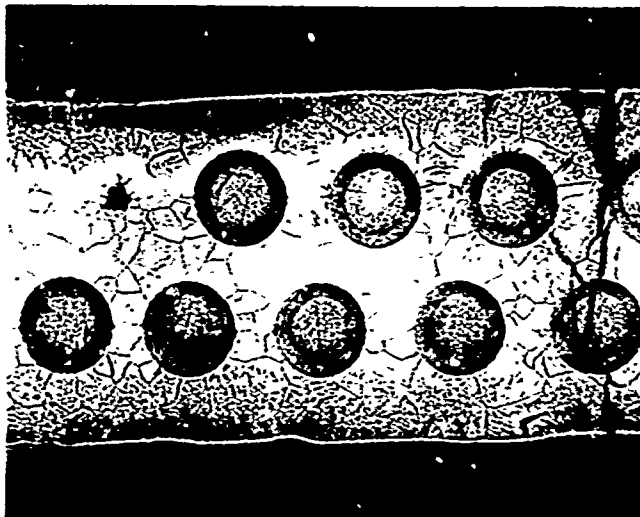
A. Pre-oxidized ~100 Hours
At 1200°F
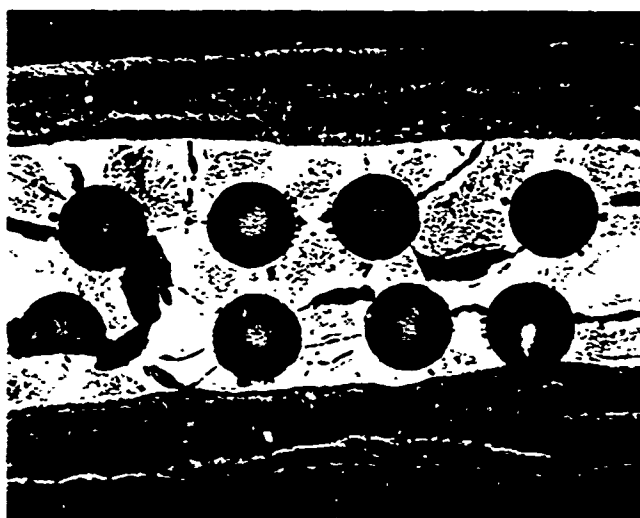
B. Oxidized Directly At 1600°F

Magnification: 50X

FIGURE 11. J-ALLOY/24W OXIDIZED ~160 HOURS AT 1600°F
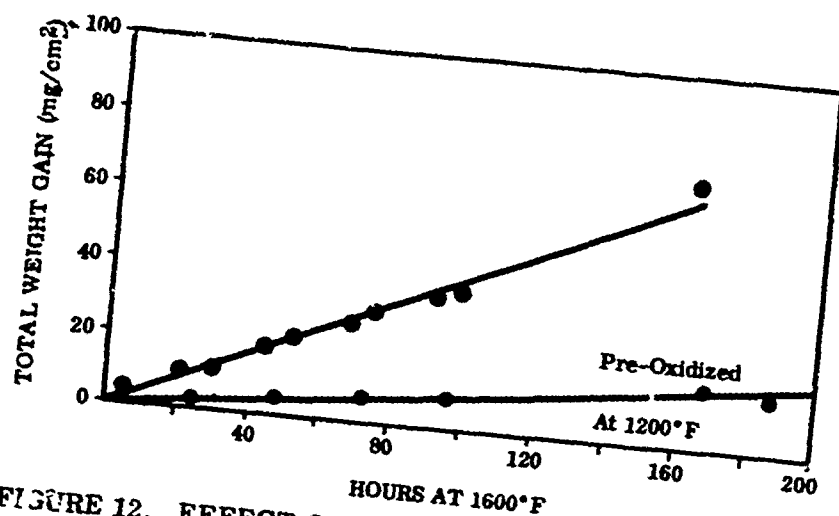
FIGURE 12.   EFFECT OF PRE-OXIDATION AT 1200°F ON
OXIDATION RATE OF J-ALLOY/W AT 1600°F
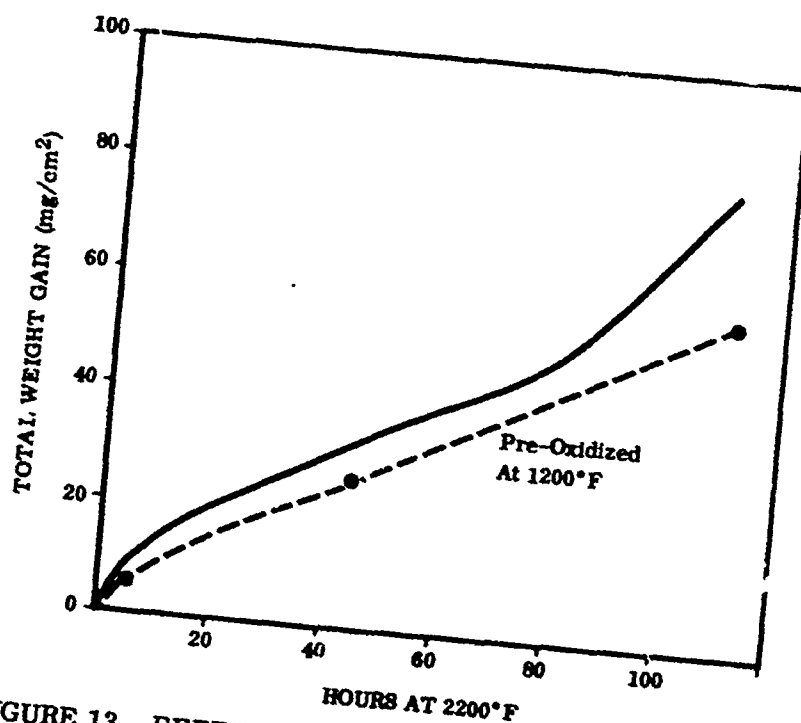
FIGURE 13.   EFFECT OF PRE-OXIDATION AT 1200°F ON
OXIDATION RATE OF J-ALLOY/W AT 2200°F

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The reason for the increased oxidation resistance of the pre-oxidized composite is not known. However, pre-oxidation at 1200°F did not enhance the oxidation resistance of the matrix alone at 1600°F for times exceeding about 80 hours. The comparison of oxidation rates at 1600°F for three-layer specimens of J-Alloy in the pre-oxidized and non-pre-oxidized conditions is shown in Figure 14.
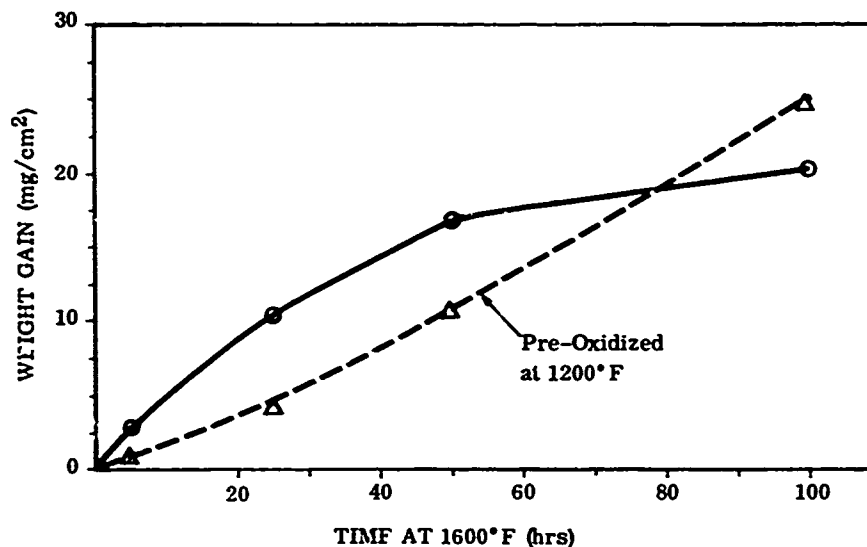
FIGURE 14. EFFECT OF PRE-OXIDATION AT 1200°F ON THE OXIDATION RATE OF J-ALLOY MATRIX; Three-Layer Specimens

4.4 THERMAL STABILITY OF THE MODEL SYSTEM

The stability of the model system was evaluated by comparing the room-temperature tensile properties of the composite and the matrix in the as-bonded and as-fabricated conditions with their tensile properties after they were held at an intermediate temperature and slowly cooled. The heat treatment would permit an aging reaction to occur if the matrix structure was unstable. The effect of the aging reaction would then be reflected by the changes in the tensile properties.

4.4.1 Stability of J-Alloy/24W

The effect of holding the J-Alloy/24W composite at 1400°F on strength and ductility at room temperature is shown in Table V. In this table, the tensile properties of an as-bonded composite (diffusion bonded at 2250°F for 30 seconds) are compared with the tensile properties of a composite specimen heat treated for 1 hour at 1400°F after bonding. The heat treatment has reduced the tensile strength of the composite by a factor of about 2, and the failure strain by a factor of 4. Metallographic

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TABLE V

CHANGE IN ROOM-TEMPERATURE TENSILE PROPERTIES INDUCED
BY AGING J-ALLOY/24W AT 1400° F

Treatment	Strain (μin./in.)		Elastic Modulus (psi x 10^6)	Tensile Strength (psi x 10^{-3})
	Proportional Limit	Failure		
As Bonded (2250°F - 30 Sec)	4500	16,000	23	170
As Bonded plus Aged 1400°F - 1 Hour & Slow Cool	4000	4,000	24	90

examination of these specimens showed that a dispersed phase had formed throughout the matrix and at the grain boundaries of the aged specimen, but there was no evidence of a dispersion in the as-bonded specimen. The microstructures are compared in Figure 15. In addition, examination of the fracture surfaces revealed that matrix failure had occurred at the grain boundaries of the aged specimen. Evidently, an aging reaction embrittles the grain boundaries to such an extent that they part at low strains and induce composite failure. Chemical analysis of the dispersion at the grain boundaries was attempted using an electron microprobe, but the extent of the dispersion at the boundaries was not sufficient to obtain a reliable analysis. However, the dispersion is believed to be a Laves MCr_2 type and, if this is true, a reduction in the chromium content of the matrix would reduce the aging reaction. Some evidence has been obtained to support this supposition, and this evidence will be presented later in this report.

4.4.2 Matrix Stability

As discussed above, the strength and ductility of the composite at room temperature are reduced when the J-Alloy/24W is aged at 1400°F. The precipitation of a chromium-rich phase might be responsible for this change in mechanical properties of the composite. To test this hypothesis, the mechanical properties of the J-Alloy and a matrix alloy with reduced chromium were determined before and after the 1400°F aging treatment. The alloy with reduced chromium is the B-Alloy (Cb-42Ti-4Cr-4Al) studied earlier in this program. As shown in Table VI, the ductility of the J-Alloy is greatly reduced (i.e., failure strain is reduced from 7 to 1 percent) when it is aged, whereas the ductility of the B-Alloy remains high after aging. These results suggest that a reduction in the chromium content of the J-Alloy might relieve the embrittlement of the composite induced by aging. This was found to be the case and alloys with reduced chromium concentration form the basis for a series of alloys tested in subsequent work and reported in Section 5.

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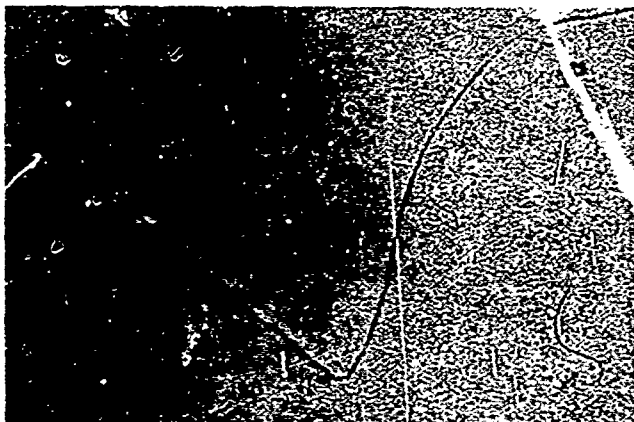
A. As Bor.ded

B. As Bonded Plus Aged 1400°F –
1 Hour and Slow Cool

Magnification: 1000X

FIGURE 15. PRECIPITATE IN J-ALLOY MATRIX INDUCED BY AGING AT 1400°F

TABLE VI

EFFECT OF AGING AT 1400°F ON TENSILE PROPERTIES
OF B- AND J-ALLOYS

| Matrix | Treatment | Strain (μ in./in.) | | Elastic Modulus (psi x 10^{-6}) | Tensile Strength (psi x 10^{-3}) |
		Proportional Limit	Failure		
J-Alloy Cb-40Ti-9Cr-4Al	2200°F - 30 Min. Furnace Cool	8500	70,000 (7%)	14	122
	2200°F - 30 Min. Furnace Cool Plus 1400°F, 1 Hour and Slow Cool	7700	10,300 (1.03%)	14	118
B-Alloy Cb-42Ti-4Cr-4Al	2200°F - 30 Min. Furnace Cool	4000	100,000 (10%)	--	98
	2200°F - 30 Min. Furnace Cool Plus 1400°F, 1 Hour and Slow Cool	4000	150,000 (15%)	--	100

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APPROACH TO ADVANCED MATRIX DEVELOPMENT

The model system, J-Alloy/W, was selected early in the program to assess the feasibility of developing a strong oxidation-resistant alloy by combining strong filaments with an oxidation-resistant matrix in a composite. This approach permitted an early determination of the potential of this application of composite technology to a practical problem. In addition, problem areas that would require modification of the model system were identified before the program effort was fully committed. This approach provided the flexibility that was required to develop a viable system with a minimum expenditure of program funds.

Candidate matrices were selected on the basis of limited screening tests that included determination of matrix oxidation resistance, matrix strength and compatibility with tungsten filaments and matrix fabricability. Two matrix alloys were found to have good potential for use with tungsten filaments. These alloys, whose compositions are similar, are J-Alloy (Cb-40Ti-9Cr-4Al) and B-Alloy (Cb-42Ti-4Cr-4Al). The former was selected as the matrix for the model system because of its somewhat greater oxidation resistance and strength. However, the B-Alloy remained a candidate matrix because the properties of both matrices had not been adequately defined by the initial screening tests.

As the properties of the J-Alloy/W composite were more completely determined, it became evident that the composition of the J-Alloy matrix would have to be modified to obtain the required combination of composite properties. In addition, the results showed that a trade-off in properties would be required since all of the desired properties could not be obtained in a single alloy.

Modifications of the J-Alloy compositions that were designed to improve matrix and composite properties included the following:

- Addition of tungsten or rhenium for improved high-temperature strength and reduction of Kirkendall porosity. It is important to know the effect of tungsten since some of this element will always be in the matrix during service because of filament-matrix interdiffusion.

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- Reduction of the chromium concentration to eliminate aging embrittlement and reduce the ductile-brittle transition temperature.

- Substitution of hafnium for all or part of the titanium. The higher melting temperature of hafnium should reduce filament-matrix interdiffusion and should increase the elevated-temperature strength of the matrix.

- Replacement of columbium by tantalum to increase matrix strength.

- Addition of carbides and silicides for grain refinement.

- Addition of vanadium to improve coating potential of the matrix.

- Addition of silicon to reduce the ductile-brittle transition temperature.

These modifications led to a matrix with reduced chromium concentration relative to J-Alloy and with tungsten and vanadium additions (Cb-40Ti-5Cr-4Al-10W-1V). Tests · the properties of this alloy showed that its use would be limited to temperatures · ow 2200° F because of matrix embrittlement induced by filament-matrix interdiffusion. However, continued study of matrix properties showed that the B-Alloy composition would be a suitable matrix for use to 2200° F. Therefore, B-Alloy with 1 percent vanadium added to enhance coatability (Cb-42Ti-4Cr-4Al-1V) was adopted at this point as the best matrix for use in future work. Coatings still must be developed for this alloy, but the silicide coating used to protect the J-Alloy is also a potential coating for this alloy (termed B-1V in this report).

The steps leading to the development of these two matrices are outlined in the following sections. These steps include a series of property measurements followed by compositional adjustments to alter these properties and a repetition of property measurements on the new matrix. Because of the large number of alloys to be tested, all of the properties were not measured for all of the alloys. Rather, selective properties were measured to determine if further tests were warranted on a particular alloy.

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ADVANCED MATRIX DEVELOPMENT

The development of improved matrices for use with tungsten filaments was initiated with preliminary oxidation screening tests. These tests were performed to determine the general effect of modification of the composition of J–Alloy on oxidation resistance. All of the comparisons were made using sliced arc-melted buttons.

The alloys surviving the preliminary oxidation screening were incorporated in an expanded series of alloys for further testing. The additional tests included the ability of the alloys to be fabricated into sheet form, the effect of aging on matrix strength and ductility, additional oxidation tests on sheet specimens, and the mechanical property tests.

6.1 PRELIMINARY OXIDATION SCREENING TESTS

The first series of tests in the advanced matrix development stage of the program were the preliminary oxidation screening tests. The purpose of these tests was to determine the general effect of matrix modifications on the oxidation rates. All of the alloy specimens (including the J–Alloy standard used for comparison) were coupons about 0.1-inch thick sliced from arc-melted buttons. Oxidation rates were determined from comparisons of weight gain at 1600 and 2000°F for times to about 100 hours. The results of these tests showed the general effect of a number of matrix modifications on the oxidation rates and permitted elimination of many of these alloys on this basis.

The composition of the J–Alloy is Cb–40Ti–9Cr–4Al. Where the alloy modification of this composition is the addition of a single element at the expense of columbium, the new composition will be designated as J–% of element added. Thus, a modified alloy in which 5 percent tungsten is substituted for part of the columbium will be designated as J–5W. This will simplify nomenclature in the diagrams and text.

The oxidation rates of the candidate matrices are compared with each other and with J–Alloy in Figures 16 and 17. There are three general types of alloys included in these results:

1. Alloys in which tungsten or rhenium replaces part of the columbium in J–Alloy, e.g., Cb–40Ti–9Cr–4Al–5W (J–5W).

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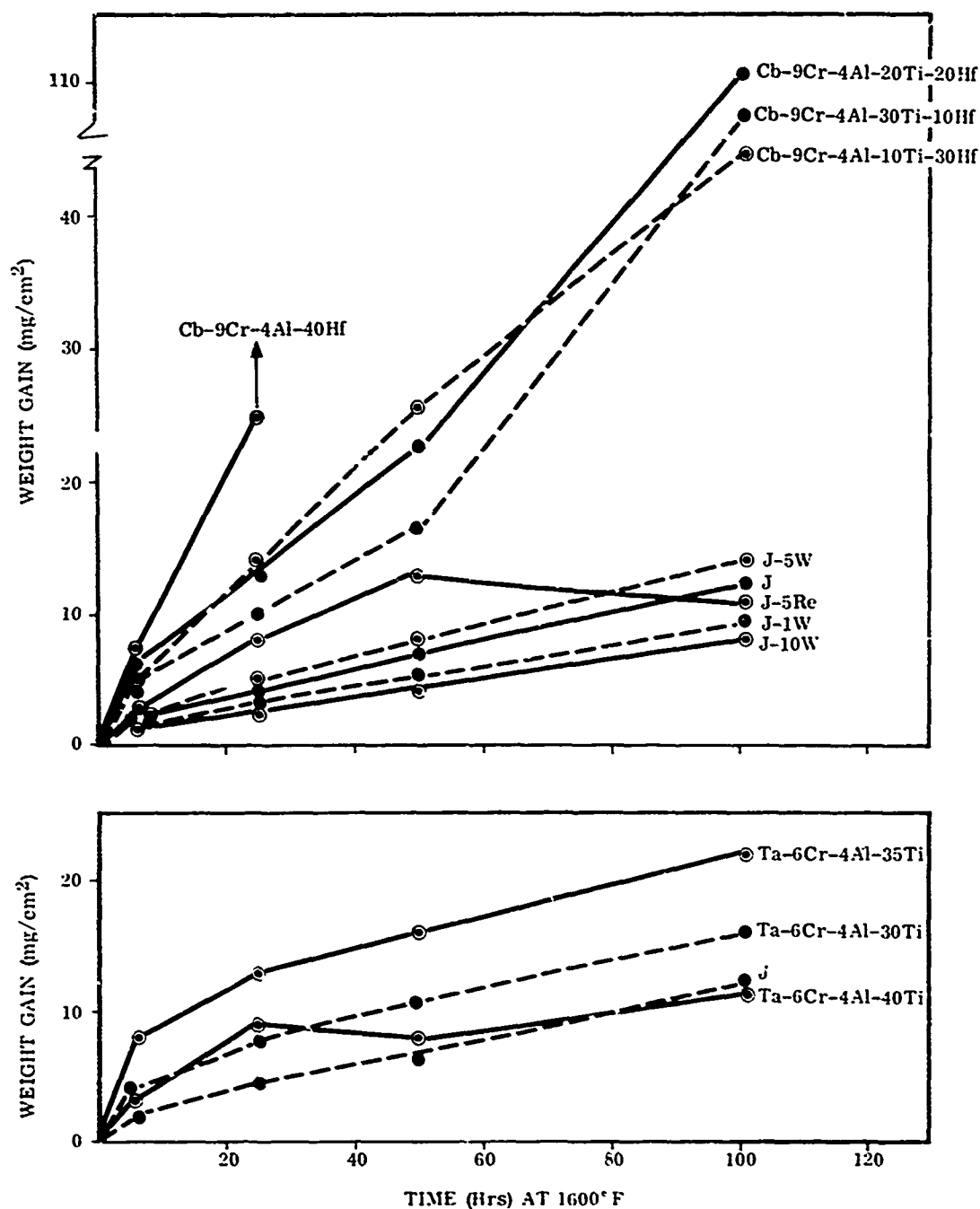
FIGURE 16. WEIGHT GAIN AS A FUNCTION OF TIME AT 1600°F FOR SOME
COLUMBIUM AND TANTALUM BASE ALLOYS; J-Alloy Designates
Cb-40Ti-9Cr-4Al; Solutes Listed Adjacent to J-Alloy in Figure
Indicate Modification of This Composite as Described in Text
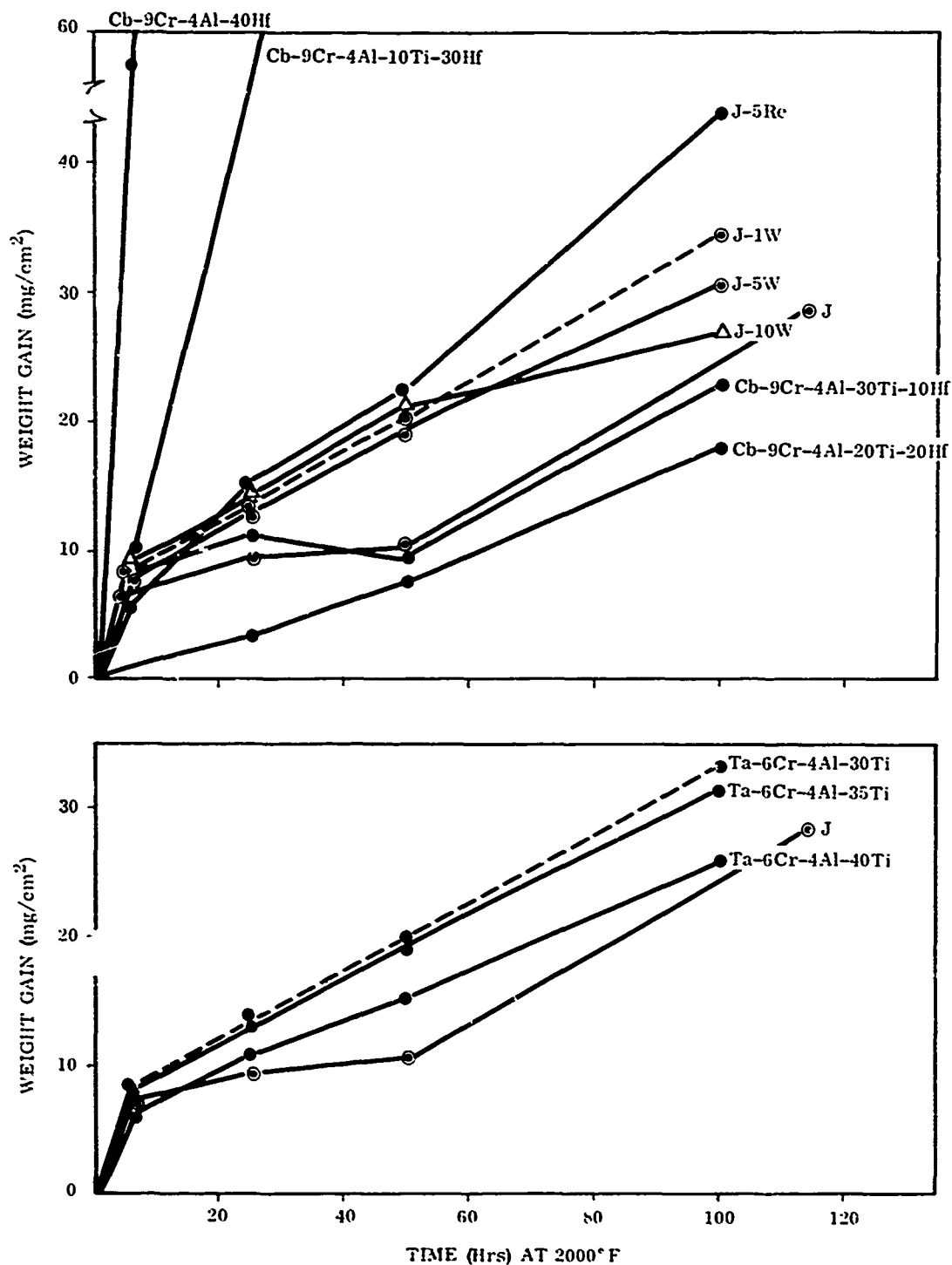
FIGURE 17. WEIGHT GAIN AS A FUNCTION OF TIME AT 2000°F FOR SOME
COLUMBIUM AND TANTALUM BASE ALLOYS; J-Alloy Designates
Cb-40Ti-9Cr-4Al; Solutes Listed Adjacent to J-Alloy in Figure
Indicate Modification of This Composition as Described in Text

2. Alloys in which hafnium is substituted for all or part of the titanium, e.g., Cb-9Cr-4Al-20Hf-20Ti.

3. Alloys in which columbium and part of the titanium are replaced by tantalum, e.g., Ta-6Cr-4Al-35Ti.

The oxidation rates of the Type 1 alloys, with the exception of J-5Re at 2000°F are close to that of J-Alloy. These results indicate that the solution of tungsten filaments in the J-Alloy matrix in composites treated for extended times at elevated temperatures is not detrimental to the oxidation resistance of the matrix. On the basis of these oxidation studies, the intentional addition of tungsten to the J-Alloy may be warranted to increase the high-temperature off-axis strength of the composite.

All of the Type 2 alloys (hafnium replacing titanium) have unsatisfactory oxidation rates at 1600°F and two of these alloys (Cb-9Cr-4Al-40Hf and Cb-9Cr-4Al-10Ti-30Hf) have unsatisfactory oxidation rates at 2000°F.

The Type 3 alloys (tantalum replacing columbium and titanium) have about the same, or slightly greater, oxidation rates as J-Alloy. Therefore, their use would have to be contingent upon other attractive properties such as increased high-temperature strength to offset the greater density of these alloys.

Since the oxidation resistance of the Type 2 alloys is unsatisfactory, these alloys were not considered further. Tests on the Type 1 alloy, J-10W, indicate that arc-melted buttons can be cold rolled into foil if they are first forged at 2200°F. Of the Type 3 alloys, only Ta-6Cr-4Al with 40 percent titanium is ammenable to cold rolling. Thus, the alloys that remain candidates for matrices with tungsten filaments are J-Alloy-W and Ta-6Cr-4Al-40Ti. These alloys, together with a number of additional alloy modifications, were studied more extensively to further define their properties. The results of these tests are described below.

6.2 FABRICATION OF POTENTIAL MATRIX ALLOYS

An important property of potential matrix alloys is their ability to be reduced from the arc-melted button to a thin foil which can be used for composite fabrication. The matrix alloys studied this period and the steps required to make foil are listed in Table VII. As shown in this table, several steps are required to reduce the alloys regardless of their composition. After arc melting, all of the alloys were forged. This is accomplished by placing the arc-melted button on edge between two anvils and reducing the button by pressure at a temperature of 2250°F. Forging is performed in a protective chamber in a dry argon atmosphere. Where double forging is indicated, the operation is repeated on the edges 90 degrees to the first forging. Some of the alloys, such as J-Alloy, could then be cold rolled while others required both hot and

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TABLE VII

FABRICABILITY OF MATRIX ALLOYS

Alloy	Number of Forgings Required at 2200°F	Type of Rolling[1]	Reduction Per Heat Treatment[2] (%)	Number of Heat Treatments Required	Results
J-Alloy And Modifications					
J-Alloy (Cb-40Ti-9Cr-4Al)	1	Cold	80	1	Very ductile
Series No. 1 (W Added and Cr Reduced)					
Cb-40Ti-9Cr-4Al-10W	2	Hot / Cold	50 / 80	2	Semi ductile
Cb-40Ti-7Cr-4Al-10W	2	Cold	50	2	Ductile
Cb-40Ti-5Cr-4Al-10W	2	Cold	80	1	Ductile
Series No. 2 (3V and Dispersion Added)					
Cb-40Ti-5Cr-4Al-3V	2	Cold	50	2	Ductile
Cb-40Ti-5Cr-4Al-10W-3V	2	Hot / Cold	50 / 80	2	Brittle
Cb-40Ti-5Cr-4Al-10W-3V-0.2 HfB$_2$	2	Hot / Cold	50 / 80	2	Brittle
Cb-40Ti-5Cr-4Al-10W-3V-0.2ZrSi$_2$	2	Hot / Cold	50 / 80	2	Brittle
Cb-40Ti-5Cr-4Al-10W-3V-0.5Y	1	–	–	–	Broken during forging
Series No. 3 (1V and Dispersion Added – Variable W)					
Cb-40Ti-5Cr-4Al-10W-1V	2	Cold	40	2	Semi-ductile
Cb-40Ti-5Cr-4Al-8W-1V	2	Cold	40	2	Semi-ductile
Cb-40Ti-5Cr-4Al-6W-1V	2	Cold	40	2	Semi-ductile
Cb-40Ti-5Cr-4Al-8W-1V-0.2HfB$_2$	2	Cold	40	2	Semi-ductile
Series No. 4 (1V and Dispersion Added with 10W)					
Cb-40Ti-5Cr-4Al-10W-1V-0.94Si	2	Cold	40	2	Ductile
Cb-40Ti-5Cr-4Al-10W-1V-0.16HfSi$_2$	2	Cold	40	2	Ductile
Cb-40Ti-5Cr-4Al-10W-1V-1HfC	2	Cold	10	3	Very brittle
Cb-40Ti-5Cr-4Al-10W-1V-2(HfSiC)	2	Cold	10	3	Very brittle
B-Alloy And Modifications					
B-Alloy (Cb-42Ti-4Cr-4Al)	1	Cold	80	1	Very ductile
Series No. 5 (1V and W Added)					
Cb-42Ti-4Cr-4Al-10W	1	Cold	80	1	Very ductile
Cb-42Ti-4Cr-4Al-4W	1	Cold	80	1	Very ductile
Cb-42Ti-4.5Cr-4Al-4W-1V	1	Cold	80	1	Very ductile
Cb-42Ti-4Cr-4Al-1V	1	Cold	80	1	Very ductile
Special Alloys					
Series No. 6					
Cb-40Ti-5Cr-10W-1V[3]	2	Cold	20	3	Semi-ductile
Ta-40Ti-6Cr-4Al	2	Cold	80	1	Ductile

1. Hot rolled at about 2000°F.
2. Heat treated for 1 hour at 2200°F.
3. Contains no aluminum.

cold rolling. Hot rolling was accomplished by encapsulating the specimens in steel tubes to protect them from surface oxidation which causes the surface of the alloy to be rough and pitted. Each alloy has its own limitation on reduction and must be heat treated (1 hour at 2200°F) before further reduction can be accomplished.

The ability of the various alloys to be rolled to sheet or foil is evaluated in the last column in Table VII. Alloys graded as ductile and semi-ductile were retained for further matrix evaluation tests while those listed as brittle were, of necessity, excluded from further testing.

Most of the alloys were based upon modifications of the J-Alloy composition because it was used in the model system and its properties were better defined than those of some of the other alloys such as B-Alloy. However, the difference in the compositions of the J- and B-Alloys is not great.

The intended purpose of most of the various compositional changes has been listed in the preceding section. The first of the two special alloys (Series 6) is a modification containing no aluminum. As will be described later, this change was made to reduce the ductile-brittle transition temperature of the fully annealed alloy. The second special alloy has a tantalum rather than a columbium base. The substitution of the tantalum-base was intended to increase the high-temperature strength of the matrix and thus the high-temperature strength of the composite for off-axis loading.

As pointed out previously, abbreviations are sometimes used to simplify identification of the alloys and to emphasize the relationship of the composition modifications to the J- or B-Alloys. Some of the alloy abbreviations used in the following sections are listed again to emphasize their meaning and relationship to the actual compositions.

Alloy Abbreviation	Composition
J	Cb-40Ti-9Cr-4Al
J-10W	Cb-40Ti-9Cr-4Al-10W
J-7Cr-10W	Cb-40Ti-7Cr-4Al-10W
B	Cb-42Ti-4Cr-4Al
B-1V	Cb-42Ti-4Cr-4Al-1V

For the alloy Cb-40Ti-7Cr-4Al-10W the abbreviation, J-7Cr-10W, shows that the composition of the new alloy differs from the original J-Alloy in its chromium and tungsten concentrations. The reduction of chromium and the addition of tungsten will, of course, change the concentration of columbium in the modified alloy with respect to J-Alloy.

The fabrication evaluation of the many alloys listed in Table VII is a first step in determining which alloys are to be retained for matrix study. Many small but significant element changes were made. In some cases these changes made very little

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difference in the fabrication method as used on the base alloy. However, the addition of tungsten created a major fabrication change when added to the J-Alloy and its modifications that contain high chromium. The result was low ductility and required double forging and initial hot rolling. As the chromium content was lowered, approaching B-Alloy and its modifications, ductility increased (as shown in Series 1 and 5).

Another alloy which caused changes in fabrication methods was vanadium. Its addition made reduction more difficult and in some alloys caused brittleness. The combination of tungsten and 3 percent vanadium was very difficult to roll even after double forging and hot rolling. When the vanadium was reduced to 1 percent, the ductility was slightly improved to the point where only double forging was required. The fabricability of the B-Alloy was not affected by the addition of 1 percent vanadium.

As shown in Table VII, small amounts of other elements were added to incorporate a dispersion in the matrices. New fabrication methods were not necessary for most of the alloys with these additions. One exception to this was the compound HfC. Addition of this compound resulted in extreme brittleness. It was at this point that a higher forging temperature (2800°F) was used to improve homogeneity, but the fabricability of the alloys was not improved by this change.

Small additions of a number of elements were added to improve the properties of the alloys. However, the additions must go into solution to be effective. Therefore, solution of the elements was always checked by radiographic examination. Due to differences in the density of each element contained in the alloy, elements not completely in solution show clearly in the radiograph. Where this was observed, alloys were remelted until all elements were in solution.

6.3 EFFECT OF AGING ON MATRIX DUCTILITY

As discussed in Section 4.4, embrittlement of J-Alloy by an aging reaction is a serious problem. When the J-Alloy/W composite or the J-Alloy matrix is held at 1400°F for an hour, the room-temperature strength and ductility are severely reduced. Failure is induced by a grain boundary precipitate that causes the boundaries to part at very low strains. The matrix cracks cause the composite to fail by serving as stress concentrators, and these cracks also expose the filaments to oxidation.

This precipitate is believed to be a chromium-rich phase and, therefore, the J-Alloy composition was modified by reducing its chromium concentration. In addition, tungsten was also added to the J-Alloy composition to increase its high-temperature strength and to reduce Kirkendall porosity formation at the interface. The latter can reduce off-axis strength if porosity is extensive. The tensile properties of these modified J-Alloy matrices were determined at room temperature before and after aging, and the results are listed in Table VIII. This is the first alloy series listed in

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TABLE VIII

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE PROPERTIES OF J-ALLOY AND MODIFIED J-ALLOY MATRICES (SERIES 1)

Alloy	Treatment[1]	Number of Tests	Strain (%)		Plastic Strain at Failure (%)	Tensile Strength (ksi)
			Proportional Limit	Failure		
(1) J-Alloy (Cb-40Ti-9Cr-4Al)	Furnace cooled	2	0.7	10.5	9.8	120
	Aged	2	0.7	2.3	1.6	119
(2) Cb-40Ti-9Cr-4Al-10W	Furnace cooled	2	--	0.44	None	108
	Aged	1	--	0.28	None	47
(3) Cb-40Ti-7Cr-4Al-10W	Furance cooled	2	1.1	14.0	12.9	126
	Aged	1	1.0	2.0	1.0	126
(4) Cb-40Ti-5Cr-4Al-10W	Furnace cooled	2	0.9	16.0	15.1	125
	Aged	1	0.9	11.0	10.1	124

1. Furnace cooled indicates that the rolled sheet was cooled in a vacuum furnace after a 30-minute heat treatment at 2200°F.

2. Aged indicates that the rolled sheet was held 1 hour at 1400°F after the 30-minute heat treatment at 2200°F.

Table VII (Series 1 - W added with reduced Cr). The plastic strain shown in Table VIII is the difference between the failure strain and the proportional limit and is used as a measure of matrix ductility.

For J-Alloy, the aging reaction reduces the plastic strain at failure to 1.6 percent. Tests on composites show that this is not enough ductility to prevent the formation of matrix cracks and to prevent premature composite failure. The addition of tungsten to the J-Alloy (second alloy in Table VIII) severely reduces ductility even before aging. After aging, this alloy failed before the elastic limit was reached and so its strength was reduced. However, the alloys with the chromium concentration reduced to 7 and 5 percent show greater ductility. Alloy number 4, with 5 percent chromium, has more than 10 percent plastic strain at failure after it is aged at 1400°F.

The effect of aging on the structure of J-Alloy was shown in Figure 15. The aged specimen has a second phase at the grain boundaries and within the matrix that is not evident in the furnace-cooled specimen. Figure 18 shows the reduction in grain boundary and matrix precipitate with reduced chromium concentration (alloys 2, 3 and 4 in Table VIII).

Table IX lists the results of the aging study for the second alloy series in Table VII. This alloy series is based upon the most ductile alloy in Series 1 which is Cb-40Ti-5Cr-4Al-10W. Three percent vanadium was added to this composition to make the matrix more receptive to coating. Dispersions or dispersion-forming

A. J-Alloy-10W
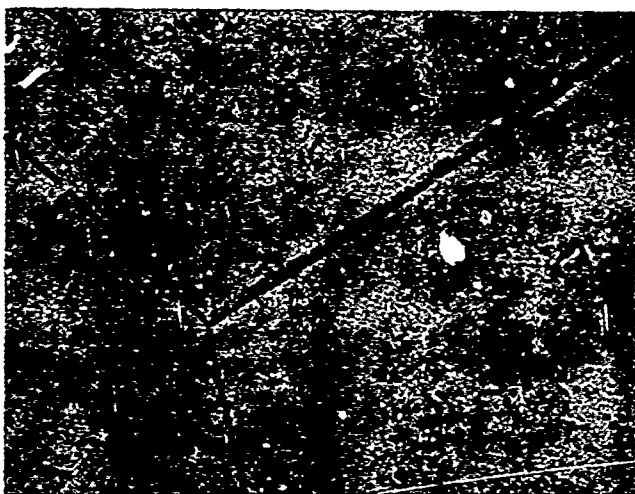
B. J-Alloy-10W-7Cr

C. J-Alloy-10W-5Cr

Magnification: 1000X

FIGURE 18. EFFECT OF CHROMIUM CONCENTRATION ON GRAIN BOUNDARY
PRECIPITATION; Alloys Were Aged for 1 Hour at 1400°F

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TABLE IX

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE PROPERTIES OF MODIFIED J-ALLOY MATRICES (SERIES 2)

Alloy	Treatment[1]	Number of Tests	Strain (%)			Tensile Strength (ksi)
			Proportional Limit	Failure	Plastic Strain at Failure	
(1) Cb-40Ti-5Cr-4Al-3V	Furnace cooled	4	0.8	9.0	8.2	122
	Aged	2	0.9	6.6	5.7	122
(2) Cb-40Ti-5Cr-4Al-10W-3V	Furnace cooled	4	—	0.68	None	102
	Aged	2	—	0.5	None	98
(3) Cb-40Ti-5Cr-4Al-10W-3V-0.2HfB$_2$	Furnace cooled	4	—	0.6	None	101
	Aged	2	—	0.6	None	98
(4) Cb-40Ti-5Cr-4Al-10W-3V-0.2ZrSi$_2$	Furnace cooled	4	—	0.75	None	122
	Aged	2	—	0.5	None	93

1. Furnace cooled indicates that the rolled sheet was cooled in a vacuum furnace after a 30-minute heat treatment at 2200°F.

   Aged indicates that the rolled sheet was held 1 hour at 1400°F after the 30-minute heat treatment at 2200°F.

elements were added for grain refinement to enhance matrix ductility and strength. As shown in Table IX, however, all of the alloys except No. 1 were very brittle, even before aging. Failure was again primarily at the grain boundaries. Even alloy No. 1, which contained no tungsten, showed a reduction in plastic strain after aging.

All of the alloys in this series contained more than one phase, and the amount of the additional phase or phases was increased by aging. Structures typical of this series are shown in Figure 19. There is the same tendency to form preferential grain boundary precipitation after aging.

The second alloy series showed that 3 percent vanadium embrittles the Cb-40Ti-5Cr-4Al-10W matrix, but that vanadium can be added to this alloy without a large loss in ductility if the tungsten is withheld. Therefore, the third alloy series contained only 1 percent vanadium and 6 to 10 percent tungsten. A dispersion was added to one alloy to determine the effect of this addition on the properties of this more ductile alloy series. The results of aging on the mechanical properties of this alloy series (No. 3) are listed in Table X. Only alloy No. 1 in this table showed no effect of aging on ductility. Therefore, this alloy (Cb-40Ti-5Cr-4Al-10W-1V) was considered a potential matrix for tungsten filaments warranting further study.

The next series of alloys was based upon the alloy Cb-40Ti-5Cr-4Al-10W-1V, which was the alloy showing the greatest ductility in Series 3 (Table X). As will be

A. Furnace Cooled

B. Aged

Magnification: 1000X

FIGURE 19. STRUCTURE OF MODIFIED J-ALLOY MATRIX TYPICAL OF
SERIES 2 AFTER FURNACE COOLING AND AFTER AGING
AT 1400°F; Matrix Composition is Cb-40Ti-5Cr-4Al-3V

TABLE X

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE
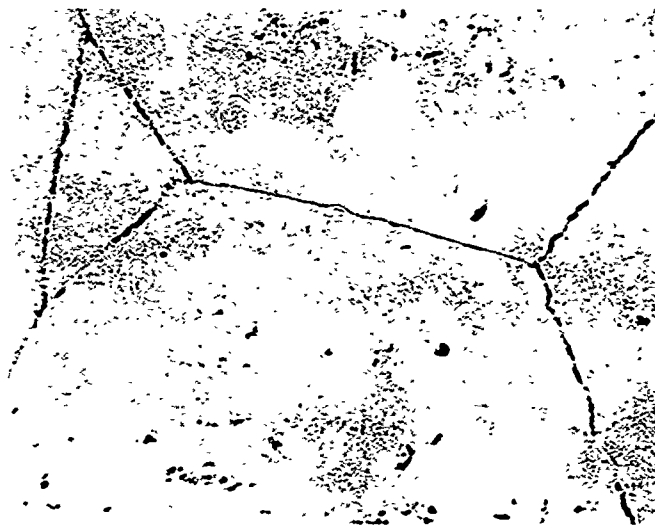PROPERTIES OF MODIFIED J-ALLOY MATRICES (SERIES 3)

Alloy	Treatment[1]	Number of Tests	Strain (%)			Tensile Strength (ksi)
			Proportional Limit	Failure	Plastic Strain at Failure	
(1) Cb-40Ti-5Cr-4Al-10W-1V	Furnace cooled	?	1.0	9.0	8.0	122
	Aged	2	1.0	9.0	8.0	123
(2) Cb-40Ti-5Cr-4Al-8W-1V	Furnace cooled	2	1.1	6.0	5.9	126
	Aged	2	0.7	0.9	0.2	99
(3) Cb-40Ti-5Cr-4Al-8W-1V-0.2HfB₂	Furnace cooled	2	0.9	9.0	8.1	129
	Aged	2	--	0.7	None	109
(4) Cb-40Ti-5Cr-4Al-6W-1V	Furnace cooled	2	0.8	11.0	10.2	128
	Aged	2	0.9	5.0	4.1	120

1. Furnace cooled indicates that the rolled sheet was cooled in a vacuum furnace after a 30-minute heat treatment at 2200°F.

   Aged indicates that the rolled sheet was held 1 hour at 1400°F after the 30-minute heat treatment.

shown later in this report, this promising alloy had a ductile-brittle transition temperature (DBTT) above room temperature after it was annealed at high temperatures. High-temperature annealing treatments destroy substructure introduced during alloy fabrication and increase grain size. Both of these factors tend to reduce ductility. Therefore, dispersions were added to this base alloy in an effort to stabilize the substructure introduced during foil preparation and to reduce grain growth.

The effect of aging on the mechanical properties of this alloy series (No. 4) are listed in Table XI. Only two alloys were tested because the other dispersion containing alloys could not be fabricated (Table VII). Unfortunately, the additions of silicon and hafnium-silicide which do lower the DBTT render the alloys susceptible to aging embrittlement.

TABLE XI

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE
PROPERTIES OF MODIFIED J-ALLOY MATRICES (SERIES 4)

Alloy	Number of Tests	Strain (%)			Tensile Strength (ksi)
		Proportional Limit	Failure	Plastic Strain at Failure	
(1) Cb-40Ti-5Cr-4Al-10W-1V-0.04Si	2	0.8	2.0	1 2	131
(2) Cb-40Ti-5Cr-4Al-10W-1V-0.16HfSi₂	2	1.0	1.5	0.5	133

Table XII lists the response of B-Alloy and some B-Alloy modifications (Series 5) to aging. The B-Alloy and its variations containing tungsten and vanadium retain good ductility after aging. The strength of the B-Alloy, which is lower than that of the J-Alloy and its modifications by about 20 ksi, is increased somewhat by the additions of tungsten and vanadium. The tolerance of this alloy series to aging shows them to be potential matrix alloys for use with tungsten filaments and, therefore, this alloy series was considered for further study.

TABLE XII

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE
PROPERTIES OF MODIFIED J-ALLOY MATRICES (SERIES 5)

| Alloy | Number of Tests | Strain (%) | | | Tensile Strength (ksi) |
		Proportional Limit	Failure	Plastic Strain at Failure	
B-Alloy (Cb-42Ti-4Cr-4Al)	1	0.4	15.0	14.6	100
(2) Cb-42Ti-4Cr-4Al-4W	2	0.96	12.1	11.1	109
(3) Cb-42Ti-4Cr-4Al-10W	2	1.0	7.7	6.7	120
(4) Cb-42Ti-4.5Cr-4Al-4W-1V	2	1.2	10.5	9.3	112

The effect of aging on one of the special alloys (Series 6) is shown in Table XIII. As will be discussed later, the other special alloy (Cb-40Ti-5Cr-10W-1V) listed in Table VII had an unsatisfactory DBTT and this eliminated it from further consideration. As shown in Table XIII, the tantalum-base alloy is very susceptible to aging embrittlement and, therefore, is not a suitable matrix alloy.

TABLE XIII

EFFECT OF AGING AT 1400°F ON ROOM-TEMPERATURE TENSILE
PROPERTIES OF A TANTALUM-BASE ALLOY (SERIES 6)

| Alloy | Treatment | Number of Tests | Strain (%) | | | Tensile Strength (ksi) |
			Proportional Limit	Failure	Plastic Strain at Failure	
Ta-40Ti-6Cr-4Al	Furnace cooled	2	0.8	11.4	10.6	125
	Aged	1	--	1.0	None	113

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6.4 OXIDATION

Oxidation tests of various alloys were conducted to determine the general effect of compositional changes on oxidation resistance and the specific oxidation resistance of certain promising alloys. Rectangular coupons (1.0 x 0.5 inch) were cut from the alloys after they had been rolled to sheet 0.012-inch thick and annealed at 2200°F for 1 hour in a vacuum. These specimens were heated in air at 1600 and 2000°F, and the weight changes were measured after various times at temperature. The weight gains due to oxidation of the various alloys were compared with each other and with those for the J- and B-Alloys to determine the effect of the composition modifications on the oxidation rate.

The results of the oxidation tests on Series 1 alloys (J-Alloy with added tungsten and reduced chromium) are shown in Figure 20. At 2000°F. the oxidation rates for this alloy series are between those for J- and B-Alloy. The addition of 10 percent tungsten to the J-Alloy composition does not change the oxidation weight gain very much at 2000°F. However, a reduction of the chromium concentration to 7 and 5 percent increases the oxidation rates toward that for the B-Alloy, which has 4 percent chromium. At 1600°F, where oxidation is much slower, the oxidation rates for all of the modified matrices are somewhat greater than the J- and B-Alloys. However, all of the oxidation rates at 1600°F are well below those at 2000°F. As reported in Section 4.3, metallographic examination of oxidation specimens showed that the weight gain profiles gave a good indication of their relative oxidation resistance.

Figure 21 compares the oxidation rates at 2000°F for Series 3 (J-Alloy with variable W, 1V and reduced Cr) with that for J-Alloy. The oxidation rate of J-5Cr-10W-1V (Cb-40Ti-5Cr-4Al-10W-1V) is the lowest of this series and, as shown in the previous section, this alloy is not embrittled by aging. It is, therefore, a candidate alloy for use as a matrix with tungsten filaments. The addition of 1 percent vanadium to the J-5Cr-10W (Cb-40Ti-5Cr-4Al-10W) to enhance coatability appears to lower the oxidation rate somewhat.

The oxidation rates at 2000°F for the Series 5 alloys (B-Alloy and modifications) are shown in Figure 22. These results show that tungsten and vanadium additions to the B-Alloy certainly do not reduce oxidation resistance but rather increase it somewhat. Tungsten will always be in the matrix of the composite during service because of filament-matrix interdiffusion and so it is important to know the effect of this element on oxidation.

The oxidation rate of the special alloy (Series 6), Ta-40Ti-6Cr-4Al, is shown in Figure 23. It oxidizes at a lower rate than J-Alloy at 1600°F and at about the same rate at 2000°F. However, as shown in the last section (Table XIII), this alloy has very low ductility after aging at 1400°F and, therefore, is not a potential matrix.
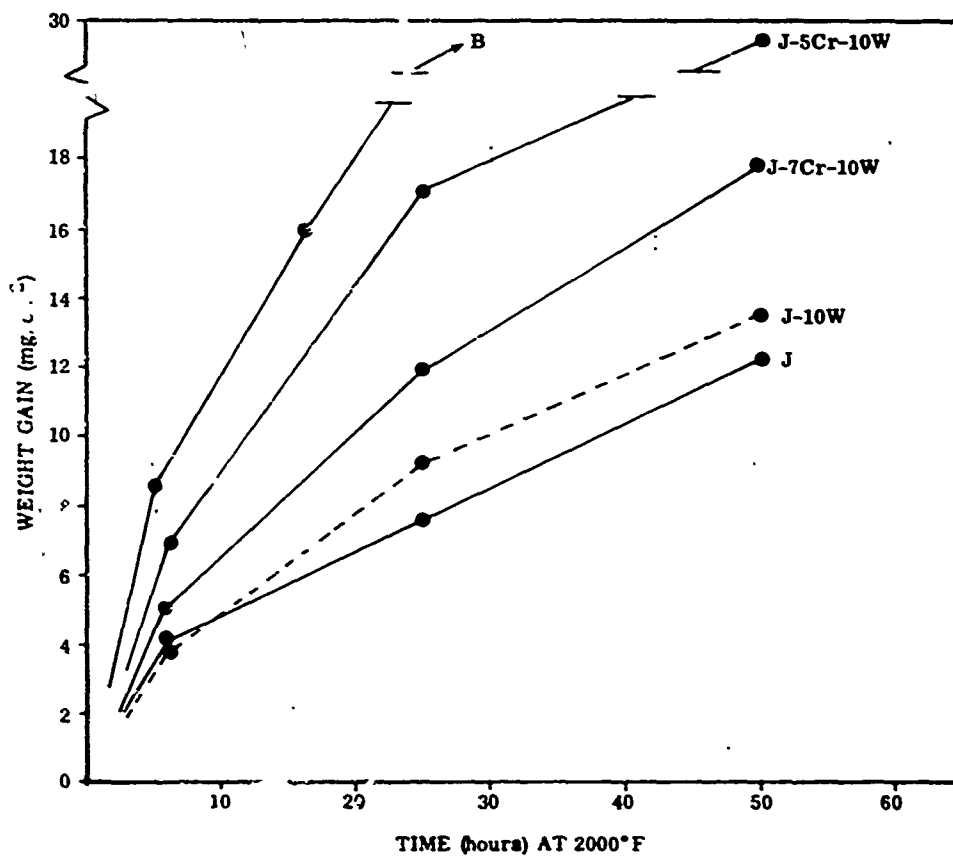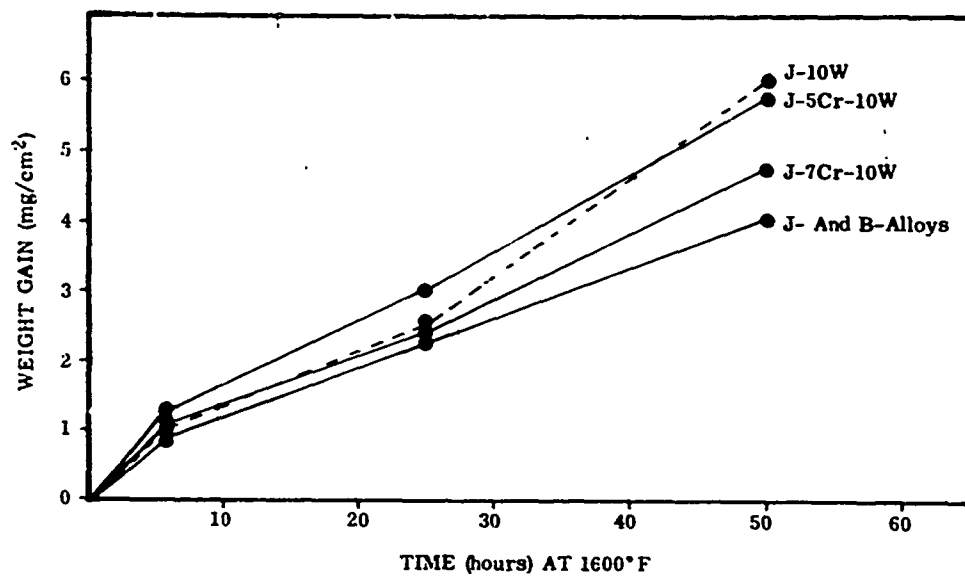
FIGURE 20. WEIGHT GAIN AS A FUNCTION OF OXIDATION TIME AT 1600 AND 2000°F FOR SOME J-ALLOY MODIFICATIONS (SERIES 1)

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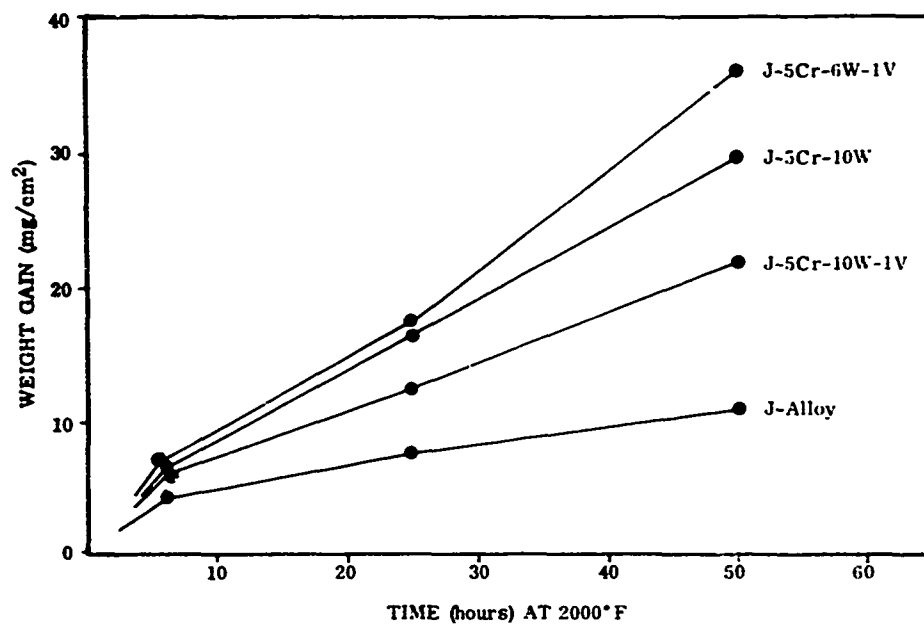
FIGURE 21. WEIGHT GAIN AS A FUNCTION OF TIME AT 2000°F FOR
SOME MODIFIED J-ALLOY MATRICES (SERIES 3)
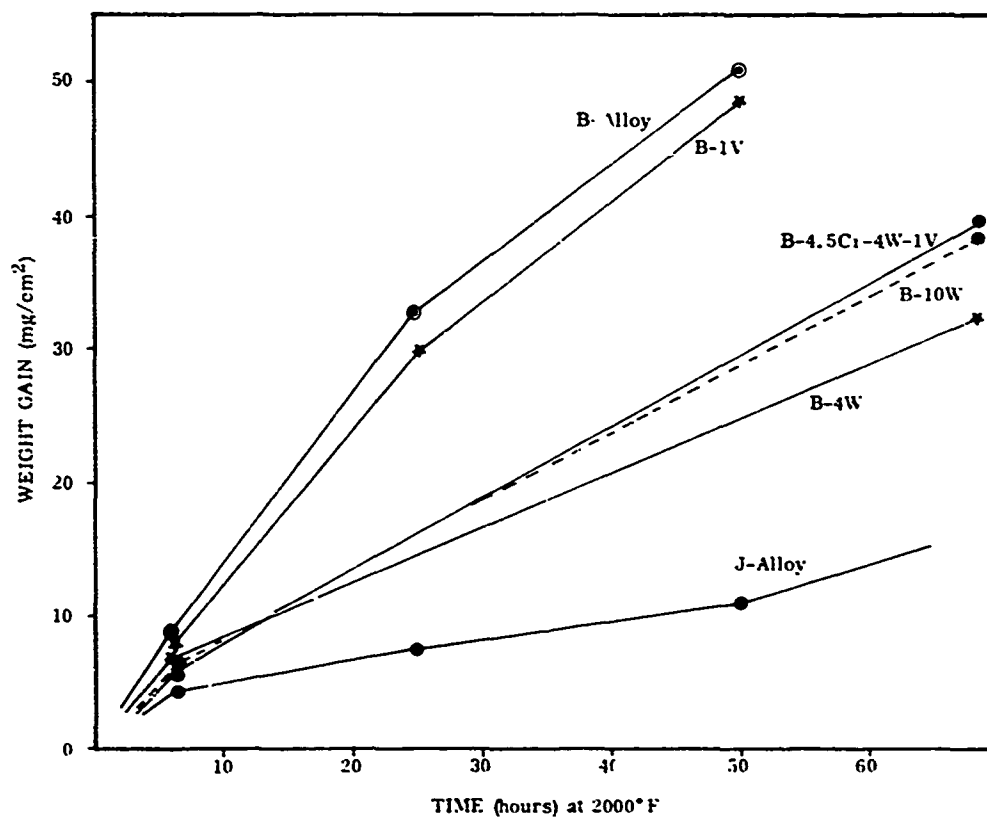
FIGURE 22. WEIGHT GAIN AS A FUNCTION OF TIME AT 2000°F FOR B-ALLOY
AND SOME B-ALLOY MODIFICATIONS (SERIES 5)
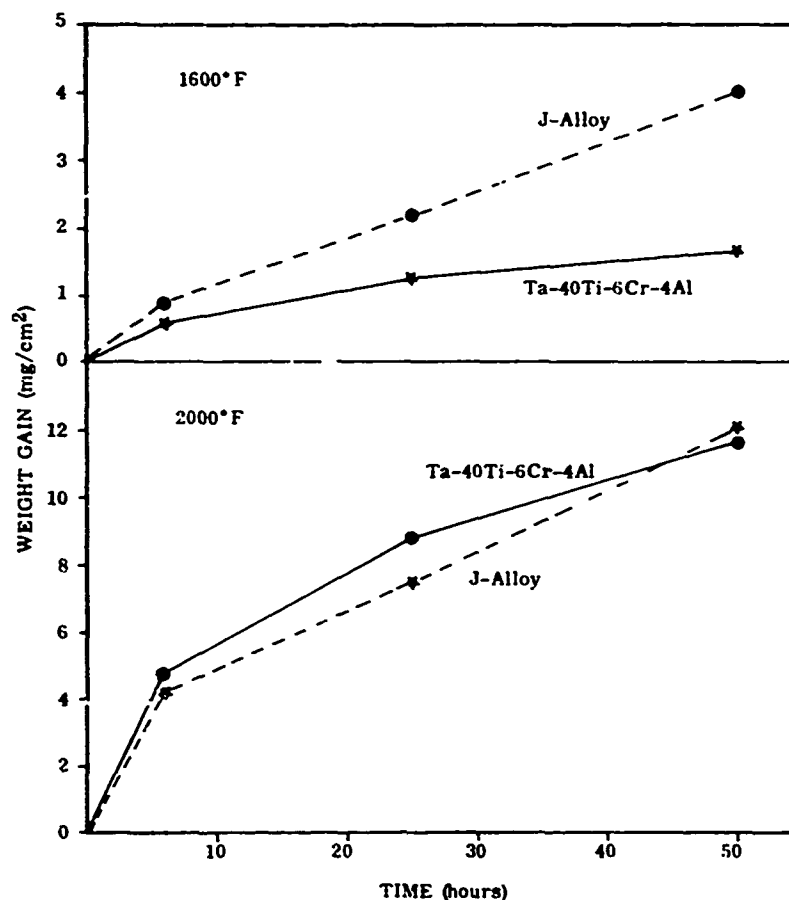
FIGURE 23. WEIGHT GAIN VERSUS OXIDATION TIME FOR
Ta–40Ti–6Cr–4Al (SERIES 6)

6.5 DUCTILE-BRITTLE TRANSITION TEMPERATURE

Most of the potential matrix alloys were ductile at room temperature after
they were rolled to foil and after they were heat treated for 1 hour at 2200° F. How-
ever, some of the alloys lost their room-temperature ductility after they were heat
treated at 2400° F. Loss of ductility after heat treatment is believed to result from an
increase in the ductile-brittle transition temperature (DBTT). This could occur be-
cause of loss of substructure generated during rolling and from grain growth when the
alloys are given the high-temperature annealing treatment. If the DBTT of the matrix
is too high, the utility of the composite could be seriously limited. Therefore, the
alloys were given further tests to determine their ductility at room temperature and
–100° F. The alloys were screened by testing matrix foils in bending and tension and
by transverse tensile testing of composites made with the various potential matrices.
The purpose of the composite tests was to determine matrix ductility after the matrix
is enriched by tungsten from the filaments. In this regard, electron microprobe

analysis of the J-Alloy/W composite showed that the tungsten concentration of the matrix at midpoint between adjacent filaments is increased to ~12 weight percent tungsten after a 100-hour heat treatment at 2200°F (Final Report, N00019-69-C-0137, November 1970).

The results of bend tests on matrices that had passed the previous screening tests are summarized in Table XIV. Flat foil specimens were bent to form a "U" shape at room temperature and at -100°F. If the specimens did not fracture, they were examined using a stereographic microscope for evidence of cracking. Ductility was classified 'good' if there was no evidence of cracking, 'fair' if there was evidence of cracking without specimen failure, and 'poor' if specimens fractured before the bend test was completed. Specimens were tested in the as-rolled condition and after heat treatments at 2200 and 2400°F.

The J-Alloy shows good room-temperature ductility in the as-rolled condition and after a 10-hour heat treatment at 2400°F. However, the ductility is only fair when tested at -100°F after a 1-hour heat treatment at 2200°F. The addition of 10 percent tungsten and 1 percent vanadium to the J-Alloy (Series 3) decreases the ductility somewhat, but a further addition of 0.04Si or 0.16 HfSi$_2$ tends to restore this ductility (Series 4). The Series 6 alloy (containing no aluminum) is not very ductile for any of the conditions tested.

The B-Alloy and all of its modifications appear to have a DBTT near or below -100°F even after heat treatments and additions of tungsten. Both of these changes tend to raise the DBTT. All of these alloys were very ductile and could be cold rolled easily with only one intermediate annealing treatment.

Some of the alloys were also tensile tested to determine their tensile strength after having been annealed for 10 hours at 2400°F. As shown in Table XV, the strength of these alloys after the 2400°F heat treatment is less than half their strength before the heat treatments (Tables VIII and X). Strains could not be measured because of the small specimen sizes, but fracture in all cases was very brittle, indicating low failure strains.

The transverse strengths of composites fabricated with some Series 1 and 3 alloys are listed in Table XVI. The composites were first given a pre-test heat treatment of 10 hours at 2400°F and then were tested at room temperature. As discussed previously, this treatment increases the tungsten concentration of the matrix due to filament-matrix interdiffusion, and this can reduce ductility. For example, the J-Alloy matrix is ductile at room temperature after the 2400°F heat treatment when tested as a foil (Table XIV) but the matrix is brittle when tested after the same treatment as a composite. This loss of ductility reduces the transverse strength from ~80 ksi to ~40 ksi. The brittle type of failure in some of these composites is shown in Figure 24.

TABLE XIV

RESULTS OF BEND TESTS ON VARIOUS MATRICES

Alloy Series	Alloy	Bend Temperature (°F)	Test Treatment	Ductility
	J-Alloy (Cb-40Ti-9Cr-4Al)	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	1 Hr-2200°F	Fair
3	Cb-40Ti-5Cr-4Al-10W-1V	75	None	Good
		75	10 Hrs-2400°F	Fair
		75	100 Hrs-2200°F	Poor
		-100	1 Hr-2200°F	Poor
4	Cb-40Ti-5Cr-4Al-10W-1V-0.04Si	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	10 Hrs-2400°F	Fair
4	Cb-40Ti-5Cr-4Al-10W-1V-0.16HfSi$_2$	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	10 Hrs-2400°F	Poor
6	Cb-40Ti-5Cr-10W-1V	75	None	Fair
		75	10 Hrs-2400°F	Poor
		-100	10 Hrs-2400°F	Poor
	B-Alloy (Cb-42Ti-4Cr-4Al)	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	1 Hr-2200°F	Good
		-100	10 Hrs-2400°F	Good
5	Cb-42Ti-4Cr-4Al-4W	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	10 Hrs-2400°F	Good
5	Cb-42Ti-4.5Cr-4Al-4W-1V	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	10 Hrs-2400°F	Good
5	Cb-42Ti-4Cr-1Al-1V	75	None	Good
		75	10 Hrs-2400°F	Good
		-100	10 Hrs-2400°F	Fair

Although the composites have numerous cracks, there is some evidence of necking in the composite with the J-5Cr-10W-1V matrix, and its transverse strength is somewhat greater than the composites with the other matrices shown in this figure.

The transverse strength of composites made with B-Alloy and modified B-Alloy matrices are listed in Table XVII. These composites were also given pre-test heat treatments of 10 hours at 2400°F before testing at room temperature. The B-Alloy has the greatest transverse strength in this series of alloys and examination of the microstructure shows that it also has the greatest ductility. As shown in Figure 25,

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TABLE XV

ROOM-TEMPERATURE TENSILE PROPERTIES OF MODIFIED J-ALLOY MATRICES

Alloy Series	Alloy	Pre-Test Heat Treatment	Number of Tests	Tensile Strength (ksi)
1	Cb-40Ti-5Cr-4Al-10W (J-5Cr-10W)	10 Hrs-2400°F	1	42
3	Cb-40Ti-5Cr-4Al-10W-1V (J-5Cr-10W-1V)	10 Hrs-2400°F	2	55
3	Cb-40Ti-5Cr-4Al-6W-1V (J-5Cr-6W-1V)	10 Hrs-2400°F	1	55

TABLE XVI

ROOM-TEMPERATURE TRANSVERSE STRENGTH OF COMPOSITES WITH MODIFIED J-ALLOY MATRICES

Alloy Series	Matrix Used In Composite	Composite Pre-Test Heat Treatment	Number of Tests	Tensile Strength (ksi)
1	J-Alloy (Cb-40Ti-9Cr-4Al)	10 Hrs-2400°F	1	40.5
1	Cb-40Ti-5Cr-4Al-10W (J-5Cr-10W)	10 Hrs-2400°F	2	34.8
3	Cb-40Ti-5Cr-4Al-10W-1V (J-5Cr-10W-1V)	10 Hrs-2400°F	2	50.0
3	Cb-40Ti-5Cr-4Al-10W-1V (J-5Cr-6W-1V)	10 Hrs-2400°F	2	33.0

the B-Alloy shows necking and evidence of slip bands in the matrix while the other alloys show a more brittle type fracture. There is some difference in the thickness of these specimens, but this is not a major factor affecting the structure shown in Figure 25. Although the modified B-Alloys are ductile after the 2400°F heat treatments when tested as foils, they tend to be embrittled after the same heat treatment when tested in composites. Embrittlement is caused by the added tungsten derived from filament-matrix interdiffusion during heat treatments.
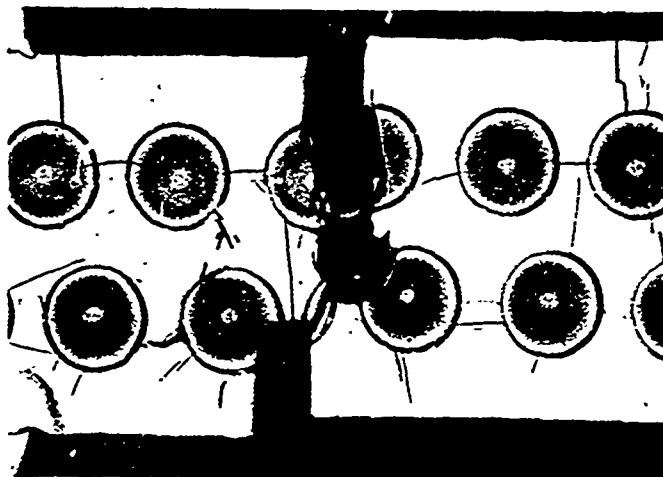
A. J-Alloy-5Cr-10W

(Cb-40Ti-5Cr-4Al-10W)

Transverse Strength: 35 ksi
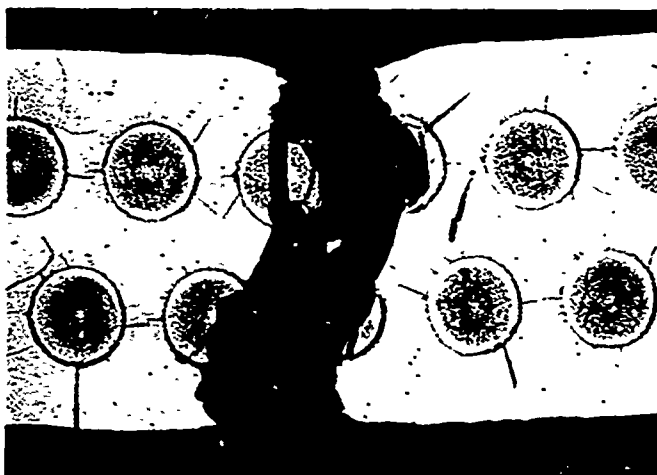
B. J-Alloy-5Cr-10W-1V
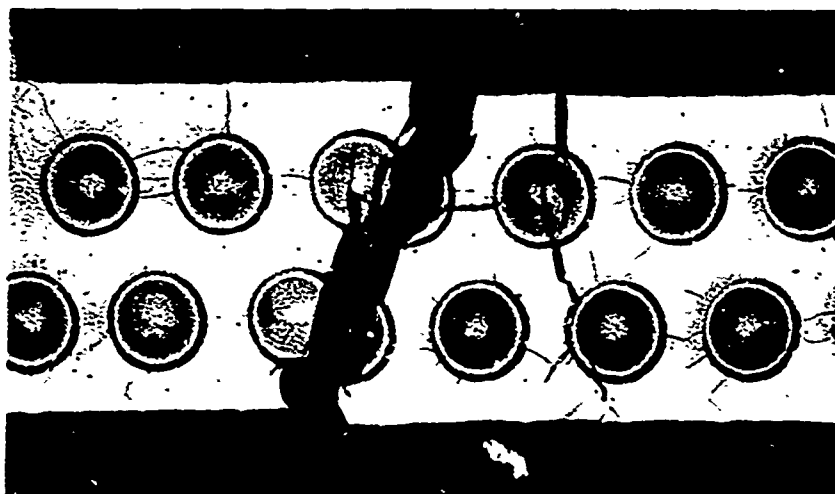
(Cb-40Ti-5Cr-4Al-10W-1V)

Transverse Strength: 55 ksi

C. J-Alloy-5Cr-6W-1V

(Cb-40Ti-5Cr-4Al-6W-1V)

Transverse Strength: 33 ksi

Magnification: 50X

FIGURE 24. TRANSVERSE TENSILE SPECIMENS TESTED AT ROOM
TEMPERATURE AFTER 10 HOURS AT 2400°F

TABLE XVII

ROOM-TEMPERATURE TRANSVERSE STRENGTH OF COMPOSITES FABRICATED FROM B-ALLOY AND MODIFIED B-ALLOY MATRICES

Alloy Series	Matrix Alloy	Number of Tests	Composite Pre-Test Heat Treatment	Tensile Strength (ksi)
5	B-Alloy (Cb-42Ti-4Cr-4Al	2	10 Hrs-2400°F	66,000
5	Cb-42Ti-4Cr-4Al-4W (B-4W)	2	10 Hrs-2400°F	36,100
5	Cb-42Ti-4Cr-4Al-10W (B-10W)	2	10 Hrs-2400°F	16,000
5	Cb-42Ti-4.5Cr-4Al-4W-1V	2	10 Hrs-2400°F	30,900
5	Cb-42Ti-4Cr-4Al-1V (B·1V)	2	10 Hrs-2400°F	59,000

6.6 OTHER MATRIX PROPERTIES

Other properties ⋅ potential matrices that were considered are elevated-temperature strength, co⋅ ⋅ bility with tungsten filaments, and formation of Kirkendall porosity in the compo ⋅ after high-temperature heat treatments. These studies have not been completed for the B-Alloy series but because of the similarity in composition of both B- and J-Alloys, it is likely that these properties will also be similar.

6.6.1 Elevated-Temperature Strength

Modified Matrices

The strength of the modified J-Alloy matrices and the tantalum alloy was determined at 2200°F. The tensile strength of these alloys at elevated temperatures is important because this property is a major factor in determining the transverse strength of the composite at elevated temperatures. The results of these tests are listed in Table XVIII. The strength of the modified J-Alloy matrices are equal or greater than the strength of the J-Alloy. The increase in strength with increased tungsten and decreased chromium is not large. In addition, the elevated-temperature strength of the tantalum alloy is surprisingly low.
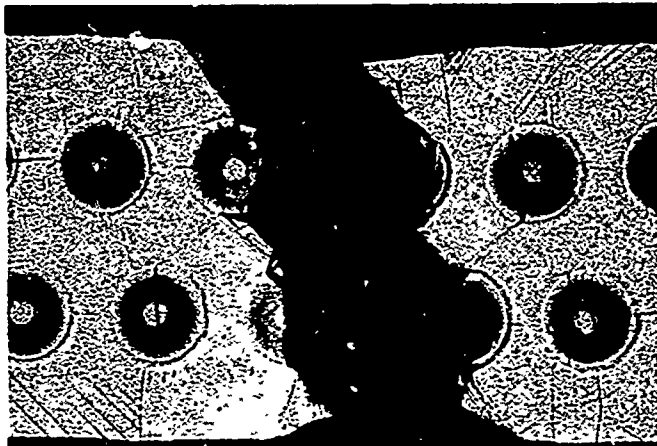
A. B-Alloy

(Cb-42Ti-4Cr-4Al)

Transverse Strength: 66 ksi
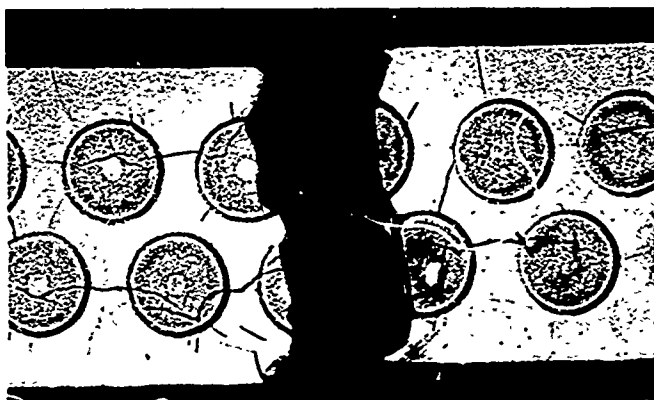
B. B-4W

(Cb-42Ti-4Cr-4Al-4W)

Transverse Strength: 36 ksi
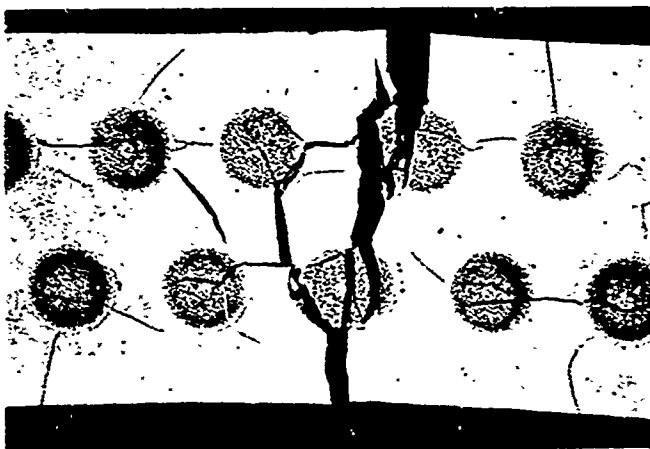
C. B-10W

(Cb-42Ti-4Cr-4Al-10W)

Transverse Strength: 16 ksi

Magnification: 50X

FIGURE 25. TRANSVERSE TENSILE SPECIMENS TESTED AT ROOM
TEMPERATURE AFTER 10 HOURS AT 2400°F (SERIES 5)
(Sheet 1 of 2)

D. B-4.5Cr-4W-1V

(Cb-42Ti-4.5Cr-4Al-4W-1V)

Transverse Strength: 31 ksi

Magnification: 50X

FIGURE 25. TRANSVERSE TENSILE SPECIMENS TESTED AT ROOM
TEMPERATURE AFTER 10 HOURS AT 2400°F (SERIES 5)
(Sheet 2 of 2)

TABLE XVIII

TENSILE DATA FOR MODIFIED J-ALLOY MATRICES AND A
TANTALUM-BASE ALLOY TESTED AT 2200°F

Alloy	Failure Strain (%)	Ultimate Tensile Strength (ksi)
J-Alloy	67	5.2
J-Alloy-10W	63	5.7
J-Alloy-10W-7Cr	77	6.4
J-Alloy-10W-5Cr	58	5.2
Ta-40Ti-6Cr-4Al	65	3.9

As discussed in Section 6.3, J-Alloy-10W-5Cr is not embrittled by aging. In addition, the transverse strength of this alloy is equal to that of the J-Alloy. Therefore, this alloy is regarded as an important potential matrix for use with tungsten filaments in composites.

Composites With Modified Matrices

The transverse strength at 2200°F of composites made with J-Alloy and some of its modifications are listed in Table XIX. As discussed previously, the transverse composite strength is largely dependent upon the matrix strength. The results show

TABLE XIX

TRANSVERSE TENSILE PROPERTIES OF MODIFIED J-ALLOY/W COMPOSITES AT 2200°F (~25 PERCENT REINFORCEMENT)

Alloy Series	Matrix Used in Composite	Composite Pre-Test Heat Treatment	Number of Tests	Failure Strain (%)	Tensile Strength (ksi)
	J-Alloy (Cb-40Ti-9Cr-4Al)	As fabricated	2	--	5.7
		10 Hrs at 2400°F	3	--	6.8
1	Cb-40Ti-5Cr-4Al-10W (J-5Cr-10W)	As fabricated	2	40	6.6
		10 Hrs at 2400°F	5	27	9.0
3	Cb-40Ti-5Cr-4Al-10W-1V (J-5Cr-10W-1V)	As fabricated	2	46	6.1
		10 Hrs at 2400°F	2	23	7.3
3	Cb-40Ti-5Cr-4Al-6W-1V (J-5Cr-6W-1V)	As fabricated	2	40	6.4
		10 Hrs at 2400°F	2	18	6.9

that the composites made with the modified matrices have higher transverse strengths than the composite made with J-Alloy, both before and after the 2400°F heat treatment. In addition, the transverse strength of all of the composites is increased by the 2400°F heat treatment. Since the transverse strength of the composite at 2200°F is increased by the tungsten and vanadium additions, inclusion of these elements in the matrix alloy should generally be beneficial to high-temperature composite strength. As pointed out earlier, tungsten will always be one of the elements in solution in the matrix after the composite is heat treated because of filament-matrix interdiffusion.

Effect of Rebonding and Heat Treatment on Transverse Strength

Composites were fabricated using the modified matrix, J-Alloy-10W-5Cr. Specimens were then prepared with about 25 volume percent filaments and subjected to transverse tensile tests at 2200°F. The specimens were tested in the as-bonded condition and after being given processing treatments to enhance transverse strength. The results of these tests are listed in Table XX. All of the transverse strengths for the composite made with the modified J-Alloy are greater than those for the composite made with J-Alloy for corresponding processing treatments. (Compare Tables IV and XX.) In addition, the strength of the composite in the as-fabricated condition exceeds that of the alloy (6.5 - 6.7 ksi for the composite and 5.2 ksi for the alloy). As shown in Table XX, the transverse strength of the composite reaches a maximum of 9 ksi at 2200°F for the specimen heat treated 10 hours at 2400°F before testing. This is the highest transverse strength at 2200°F attained for these alloys with tungsten filaments.

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TABLE XX

EFFECT OF PROCESSING TREATMENT ON THE TRANSVERSE STRENGTH OF MODIFIED J-ALLOY MATRIX/W COMPOSITE AT 2200°F

The Modified Matrix Composition Is Cb-40%:-5Cr-4Al-10W

| Pre-Test Heat Treatment	Specimen Number	Failure Strain (%)	Ultimate Tensile Strength (ksi)
As-fabricated	1	30	6.5
	1A	50	6.7
1 hour, 2400°F	2	40	7.8
1 hour, 2400°F and rebond	3	30	8.6
10 hours at 2400°F	5	27	9.0
1 hour, 2400°F, rebond plus 9 hours at 2400°F	4	30	8.5

6.6.2 Compatibility and Porosity

Some tests were conducted to determine the general effect of tungsten and vanadium additions to the J- and B-Alloys on compatibility and on Kirkendall porosity since many of the alloy modifications contained these elements. As shown in Figures 26 and 27, neither of these elements affects the compatibility of the composites subjected to a heat treatment of 10 hours at 2400°F.

The addition of tungsten to the matrix, however, does seem to reduce Kirdendall porosity resulting from unequal filament-matrix diffusion. As shown in Figure 28, the composite with the modified J-Alloy matrix containing tungsten has less porosity after heat treatment than the composite with the J-Alloy matrix.

6.6.3 Cyclic Heat Treatments

Coated composite specimens with a B-1V matrix were subjected to cyclic heat treatments in a simulated rig tester. Specimens were given 1-hour cycles at 2000°F with about 40 seconds required for heating or cooling. The specimens tested were composed of two layers of filaments similar to those shown earlier in this report. Various coatings were applied, but a simple silicide coating yielder the best results.
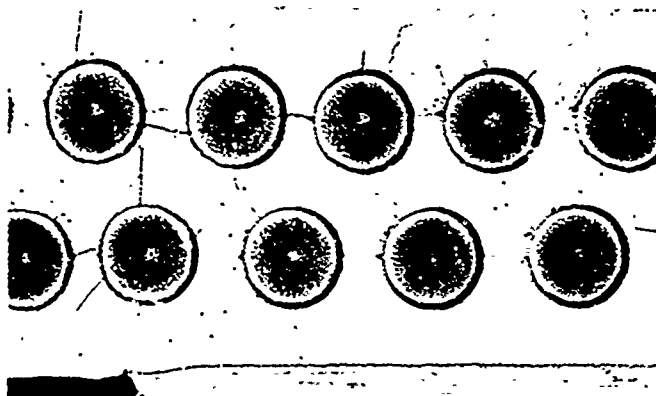
Magnification: 50X

FIGURE 26. COMPOSITE WITH TUNGSTEN FILAMENTS AND A
Cb-40Ti-5Cr-4Al-10W-1V (J-5Cr-10W-1V) MATRIX
SHOWING FILAMENT-MATRIX COMPATIBILITY
AFTER 10 HOURS AT 2400°F
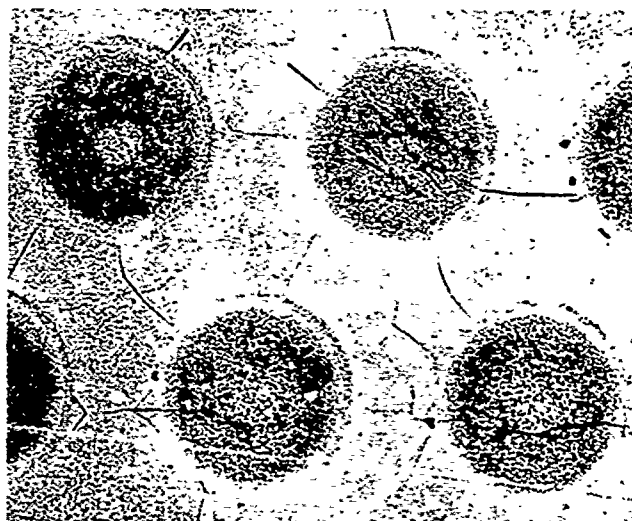
Magnification: 100X

FIGURE 27. COMPOSITE WITH TUNGSTEN FILAMENTS AND A
Cb-42Ti-4.5Cr-4Al-4W-1V MATRIX SHOWING
FILAMENT-MATRIX COMPATIBILITY AFTER
10 HOURS AT 2400°F

A. J-Alloy/W
   After 10 Hours at 2400°F
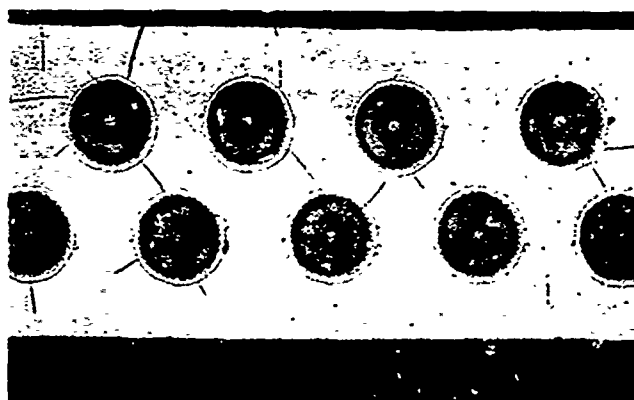
B. J-Alloy-5Cr-10W/W
   After 10 Hours at 2400°F

FIGURE 28. J-ALLOY/W AND J-5Cr-10W/W COMPOSITES AFTER
10 HOURS AT 2400°F SHOWING A DIFFERENCE IN
POROSITY (MAGNIFICATION: 50X)

Initially, the specimens subjected to thirty cycles at 2000°F were found to contain cracks in the coating. However, cracking was greatly reduced by increasing the thickness of matrix cover 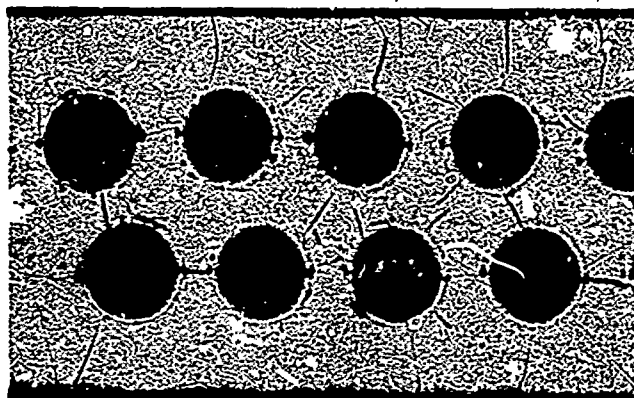over the filaments. Work to improve the cyclic oxidation resistance of this composite is still underway. Results thus far indicate that the cyclic oxidation life can be significantly extended by carefully controlling the thickness of the silicide coating and the matrix cover over the filaments.

6.7 SUMMARY OF ADVANCED MATRIX DEVELOPMENT

The results of these alloy evaluation studies are summarized in Table XXI. The properties of the alloys that were investigated are listed across the top of the table, and the potential matrix alloys for use with the W-3Re filaments are listed vertically along the left side of the table. Crosses are used to grade the alloys with respect to the properties tested. All of the properties of some alloys were not tested because they were disqualified before all tests were completed. The grades, very

TABLE XXI

SUMMARY OF STUDY OF ALLOYS FOR MATRICES WITH W-3Re FILAMENTS

Symbols Under Alloy Properties are as Follows: XXX = Very Satisfactory; XX = Satisfactory; X = Marginal

Alloy	Fabrica-bility	Aging Embrit-tlement	Oxidation Resistance	Ductile-Brittle Transition Temperature		Compati-bility	Porosity	High Temper-ature Strength	Remarks
				Matrix	Composite After Heat Treat				
J-Alloy (Cb-40Ti-9Cr-4Al)	XXX	X	XXX	XX	X	XXX	XX	XXX	Unsatisfactory DBTT and aging embrittlement
Series 1 (W added and Cr reduced)									
Cb-40Ti-9Cr-4Al-10W	XX	X	XXX			XXX	XXX	XXX	Embrittled by aging
Cb-40Ti-7Cr-4Al-10W	XX	X	XX			XXX	XXX	XXX	Embrittled by aging
Cb-40Ti-5Cr-4Al-10W	XX	XX	XX	X	X	XXX	XXX	XXX	Potential matrix alloy for use below 2200°F
Series 2 (3V and dispersion added)									
Cb-40Ti-5Cr-4Al-3V	XX	XX							Questionable fabricability and aging properties
Cb-40Ti-5Cr-4Al-10W-3V	XX	X							Embrittled by aging
Cb-40Ti-5Cr-4Al-10W-3V-0.2HfB2	XX	X							Embrittled by aging
Cb-40Ti-5Cr-4Al-10W-3V-0.2ZrSi2	XX	XX							Embrittled by aging
Cb-40Ti-5Cr-4Al-10W-3V-0.5Y	X								Embrittled by aging
Series 3 (3V and dispersion added-variable W)									
Cb-40Ti-5Cr-4Al-10W-1V	XX	XXX	XXX	X	X	XXX	XXX	XXX	Potential matrix alloy for use below 2200°F
Cb-40Ti-5Cr-4Al-8W-1V	XX	X				XXX	XXX		Embrittled by aging
Cb-40Ti-5Cr-4Al-6W-1V	XX	XX	XX	X		XXX	XXX	XXX	Unsatisfactory DBTT and questionable aging
Cb-40Ti-5Cr-4Al-8W-1V-0.2HfB2	XX	XX	XX			XXX	XXX		Embrittled by aging
Series 4 (1V and dispersion added with 10W)									
Cb-40Ti-5Cr-4Al-10W-1V-0.04Si	XX	X		XX		XXX	XXX		Embrittled by aging
Cb-40Ti-5Cr-4Al-10W-1V-0.16HfSi2	XX	X		XX		XXX	XXX		Embrittled by aging
Cb-40Ti-5Cr-4Al-10W-1V-1HfC	X								Can not be fabricated
Cb-40Ti-5Cr-4Al-10W-1V-2HfSiC	X								Can not be fabricated
B-Alloy (Cb-42Ti-4Cr-4Al)	XXX	XXX	X	XXX	XX	XXX	XX	XX	Potential matrix for high temperature use
Series 5 (1V and W added)									
Cb-42Ti-4Cr-4Al-10W	XXX	XX	XX	XX	X	XXX	XXX	XX	Unsatisfactory DBTT after heat treat
Cb-42Ti-4Cr-4Al-4W	XXX	XX	XX	XX	X	XXX	XXX	XX	Unsatisfactory DBTT after heat treat
Cb-42Ti-4.5Cr-4Al-4W-1V	XXX	XX	XX	XX	X	XXX	XXX	XX	Unsatisfactory DBTT after heat treat
Cb-42Ti-4.5Cr-4Al-1V	XXX	XX	X	XXX	XX	XXX	XX		Matrix selected for further work
Series 6 (Special Alloys)									
Cb-40Ti-5Cr-10W-1V	XX	X	XXX	X		XXX	XX	XX	DBTT above room temperature
Ta-40Ti-6Cr-4Al	XX	X	XXX			XXX	XX	XX	Severely embrittled by aging

satisfactory (XXX), satisfactory (XX), and marginal (X), have considerable latitude within each of the grades, and therefore, the remarks column is used to further clarify alloy properties. The system serves to summarize results in a concise way without the complexities that would arise from use of a more discriminating grading system.

The J-Alloy has many desirable properties (including excellent oxidation resistance). However, the embrittlement by aging and after the composite is heat treated at high temperatures would place serious restrictions on the use of a composite with this alloy as a matrix. In the first series, the alloy Cb-40Ti-5Cr-4Al-10W is judged to be the best potential matrix for use with tungsten filaments. Its limitation is a relatively high ductile-brittle transition temperature (DBTT) after the matrix or composite is heat treated at high temperatures. This can be avoided by restricting composite use to temperatures below about 2200°F. The exact limits with respect to the temperature and time to avoid this embrittlement have not been defined because of the time that would be required to extend this study.

None of the second series of alloys are judged to be suitable alloys for use as matrices because of severe aging embrittlement or questionable fabricability. The first alloy in this series could be rolled into foil easily, but it had a tendency to split when it was subjected to roll grooving. Grooves are required for proper placement of filaments in composite fabrication.

In the third series, the alloy Cb-40Ti-5Cr-4Al-10W-1V is considered the best potential matrix, but its use would also be restricted to temperatures somewhat below 2200°F because of a relatively high DBTT after heat treatment. It has the same composition as the alloy selected from Series 1, but contains 1 percent vanadium.

None of the Series 4 alloys are candidate matrices because of difficulty in fabrication or aging embrittlement. Two of the alloys could not be rolled because of the very brittle condition of the arc-melted buttons for these compositions.

The B-Alloy is a potential matrix for use with tungsten filaments to temperatures to 2200°F. It is not embrittled by aging and has a DBTT below room temperature. Althouth its oxidation resistance is lower than most of the other alloys tested, its oxidation resistance is probably adequate since the composite will be used in the coated condition. Only fail-safe oxidation resistance is required. This same alloy with 1 percent vanadium added to enhance coatability (Series 5) is also a potential matrix for use to 2200°F. Both of these alloys will be coated to further screen them for use as matrices in the composite. The other Series 5 alloys are not suitable matrices but do show the effect of tungsten additions to B-Alloy on the various properties. This is important information, since the composite matrix will be enriched by tungsten from the filaments when the composite is used at high temperatures.

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The special alloys that were tested (Series 6) are not suitable as matrices because of aging embrittlement as unsatisfactory DBTT. Although the tantalum-base alloy has excellent oxidation resistance, it is severely embrittled by aging.

7

SUMMARY OF PROPERTIES OF OXIDATION-RESISTANT COMPOSITE

The results of this program to develop a strong oxidation-resistant alloy through use of composites are summarized in this section. The outline includes data presented previously (First Annual Report, January 1970 and Final Report, November 1970), and also presents the current status in a continuing program.

This summary includes data derived for composites using the B-1V matrix (Cb-42Ti-4Cr-4Al-1V) as well as data derived using the J-Alloy matrix (Cb-40Ti-9Cr-4Al) with W-3Re filaments. Therefore, both matrices are designated as Cb(Alloy) in this summary. This approach is used because the two matrices have very similar mechanical properties with the exception of the greater low-temperature ductility of B-1V matrix. In effect, the B-1V matrix is like a J-Alloy matrix with greater ductility, and this is why B-1V matrix is preferred. In any event, sufficient experimental work has been done to allow integration of data for the two matrices to show the mechanical property behavior to be expected for the preferred B-1V/W composite.

The experimental data in the outline are for the composite with 25 volume percent tungsten filaments, but results are also presented for 40 volume percent tungsten filaments because this is the packing density used in composite fabrication. The two-layer 25 volume percent tungsten composite used in this study will approach the theoretical 40 percent as the number of filament layers increases. Engineering estimates are shown as lines in the figures or are indicated in tables by notations. The projected results for 40 percent tungsten filaments are for the most part rule-of-mixtures calculations.

7.1 TENSILE PROPERTIES

The tensile properties of uncoated Cb(Alloy)/W composites are shown graphically in Figure 29 and are listed in Tables XXII and XXIII. The elevated-temperature data were obtained by testing specimens in an inert atmosphere.

Figure 29 shows the experimentally determined strength of the Cb(Alloy)/ 27%W composite to 2300°F and the calculated strength of the composite with 40 percent tungsten over the same temperature span. The strength of the composite tends to
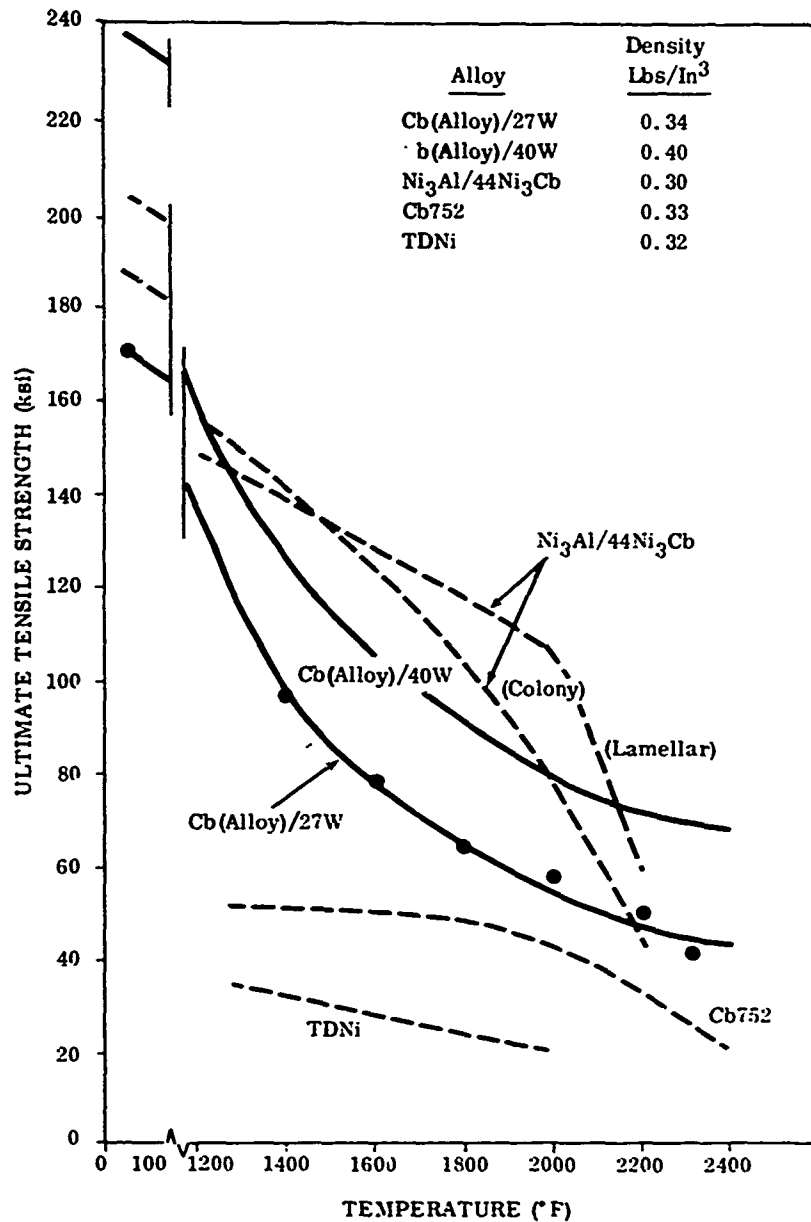
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FIGURE 29. LONGITUDINAL TENSILE STRENGTH VERSUS TEST
TEMPERATURE FOR Cb(ALLOY)/W AND SOME OTHER
ALLOYS; The Data are Calculated for 40%W in the
Composite Because this is the Packing Density Presently
Used

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TABLE XXII

LONGITUDINAL TENSILE PROPERTIES OF Cb(ALLOY)/W COMPOSITE

Volume Percent Filaments In Composite	Room Temperature			2200 °F		
	Elongation (%)	Elastic Modulus (psi x 10⁻⁶)	Ultimate Tensile Strength (ksi)	Elongation (%)	Elastic Modulus (psi x 10⁻⁶)	Ultimate Tensile Strength (ksi)
25	1.6	24	173	12	13[1]	50
40[2]	1.6	31	238	12	20	80

1. Calculated from matrix and filament data.
2. Calculated from matrix and filament data or from results for 25%W.

TABLE XXIII

TRANSVERSE TENSILE PROPERTIES OF Cb(ALLOY)/W COMPOSITES

Volume Percent Filaments In Composite	Room Temperature			2200°F		
	Elongation (%)	Elastic Modulus (psi x 10⁻⁶)	Ultimate Tensile Strength (ksi)	Elongation (%)	Elastic Modulus (psi x 10⁻⁶)	Ultimate Tensile Strength (ksi)
25	50	22	85	>10	9[1]	6
40[2]	50	25	55	>10	11	4

1. Calculated from matrix and filament data.
2. Calculated from matrix and filament data or estimated from results for 25%W.

be less sensitive to temperature at higher temperatures because strength at high temperatures, is determined primarily by the tungsten filaments.

The strengths of some other alloys are also shown for comparison in Figure 29. The data for $Ni_3Al/44Ni_3Cb$ are given for two types of microstructures – colony and lamellar. This composite is very strong at intermediate temperatures but loses strength rapidly above 2000°F because of its low melting point (2340°F). In contrast, the melting point of the matrix (and, of course, the filaments) in the Cb(Alloy)/W composite is above 3200°F.

The longitudinal and transverse tensile properties for the composite at room temperature and at 2200°F are listed in Tables XXII and XXIII. At high temperatures, the longitudinal tensile properties are determined primarily by the tungsten filaments, whereas the transverse tensile properties are determined primarily by the matrix.

7.2 CREEP AND STRESS RUPTURE

The creep properties for the composite are shown in Figures 30 through 35. Figure 30 gives the experimental data for Cb(Alloy)/24W at 2000°F and the calculated results for a 40 percent tungsten composite. Also shown are the creep-rupture properties for Cb752 and TD Nickel. Figure 31 shows the stress for 100-hour failure at 2000°F as a function of the volume percent filaments. The solid line extrapolated from the data points indicates that a 40 volume percent composite would have a 100-hour failure stress of over 40 ksi.

The stress-rupture properties of the coated Cb(Alloy)/W composite are compared with the stress-rupture properties of other alloys on a specific strength basis, in Figure 32. The best competitive material is the $Ni_3Al/44Ni_3Cb$ composite, but at high temperatures for long times, the rupture stress decreases because of structural instability.

Figures 33 and 34 are comparisons of the 100-hour stress-rupture strength of the Cb(Alloy)/W with some other oxidation-resistant alloys. The $Ni_3Al/44Ni_3Cb$ composite shows the greatest temperature dependence, and SiC yields the best stress-rupture results on a specific strength basis. However, silicon carbide has the lowest ductility of any of the materials shown. Creep curves for coated Cb(Alloy)/W specimens tested in air are shown in Figure 35. All of the specimens show 3 percent creep strain or more before failure.

7.3 STABILITY OF COMPOSITE

In many composite systems, heat treatments result in an interface interaction that severely degrades the mechanical properties of the composites. This possibility
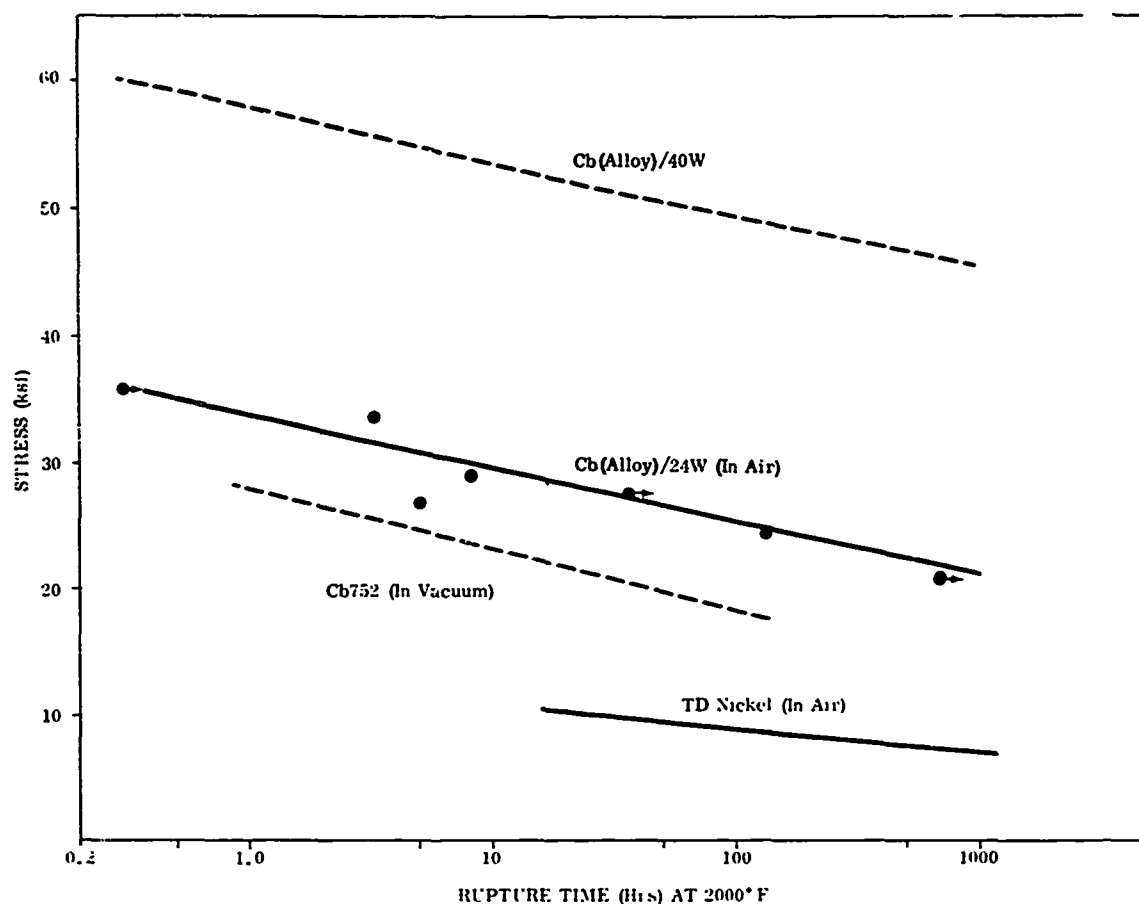
FIGURE 30. STRESS-RUPTURE DATA AT 2000°F FOR Cb(ALLOY)/W COMPOSITE
AND SOME OTHER ALLOYS; The Data are Calculated for 40%W in the
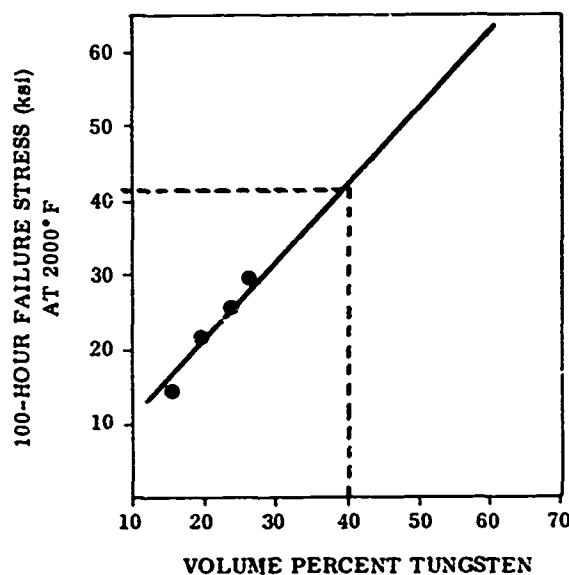Composite Because this is the Packing Density Presently Used

FIGURE 31. STRESS FOR FAILURE IN 100 HOURS AT 2000°F AS A FUNCTION
OF THE VOLUME PERCENT OF TUNGSTEN FILAMENTS IN THE
COMPOSITE; Forty Volume Percent (Dashed Line) is the Packing
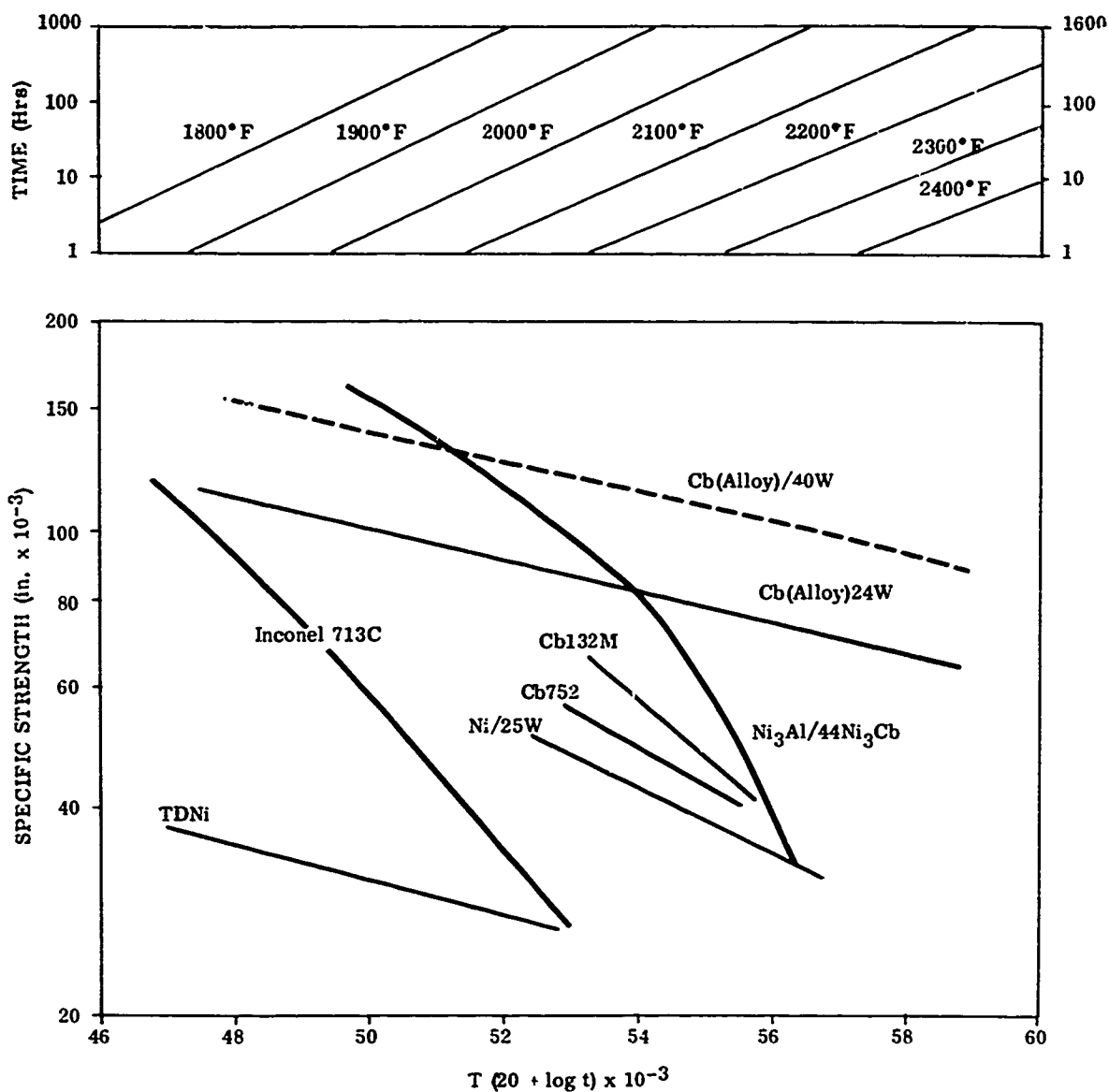Density Presently Used in the Composite

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FIGURE 32. STRESS–RUPTURE DATA FOR SOME HIGH–STRENGTH
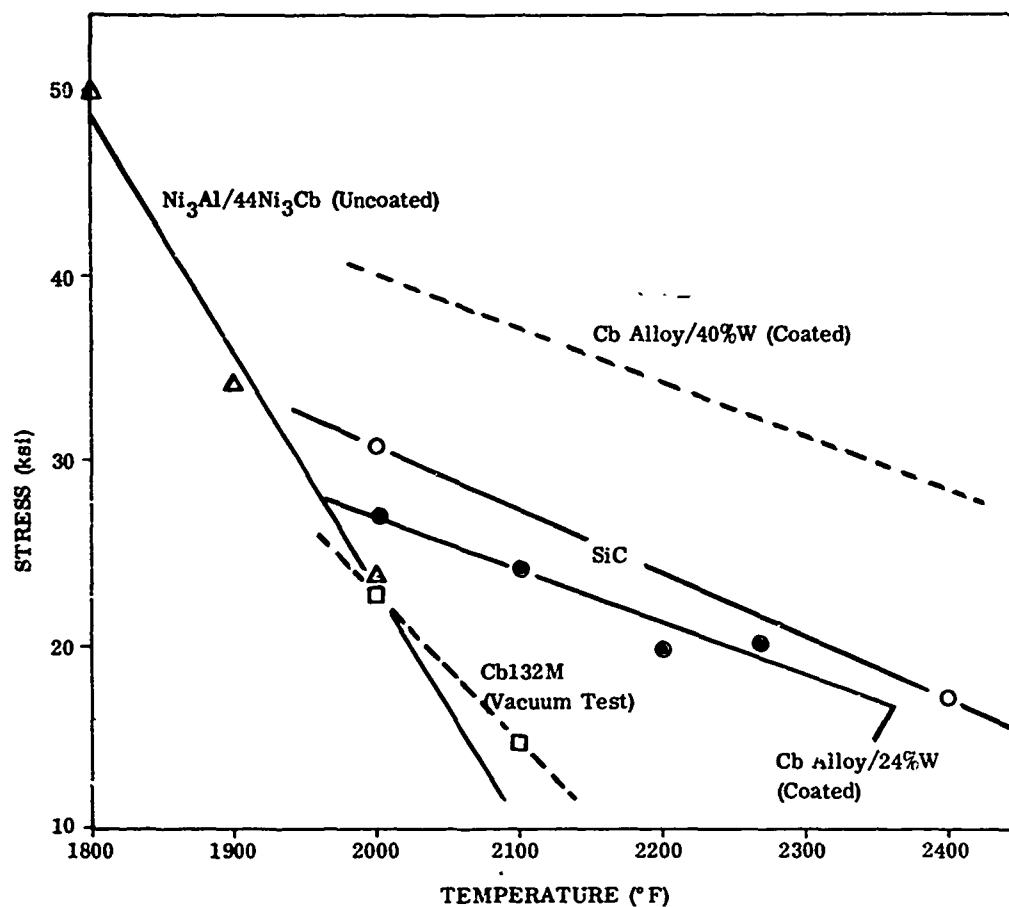ALLOYS COMPARED ON A SPECIFIC STRENGTH BASIS

FIGURE 33. STRESS FOR FAILURE IN 100 HOURS FOR SOME
HIGH-STRENGTH MATERIALS; With the Exception
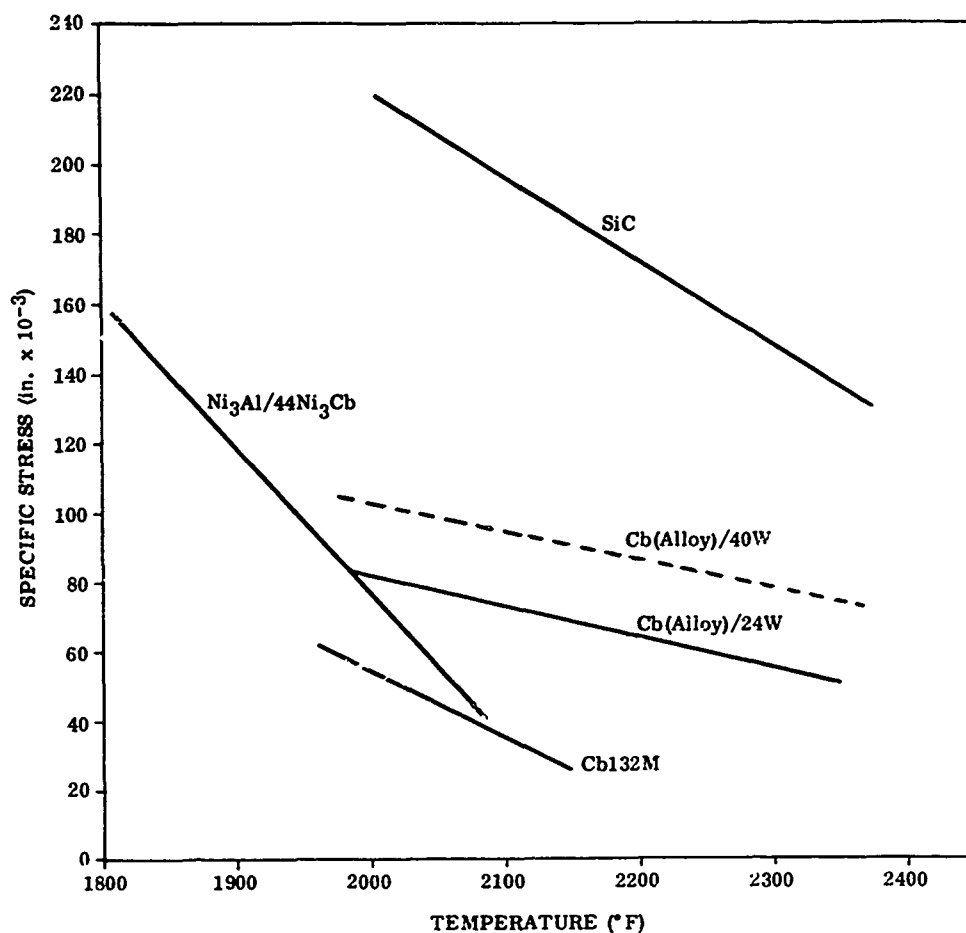of Cb-132M, Results are for Tests in Air

FIGURE 34. SPECIFIC STRESS FOR FAILURE IN 100 HOURS FOR
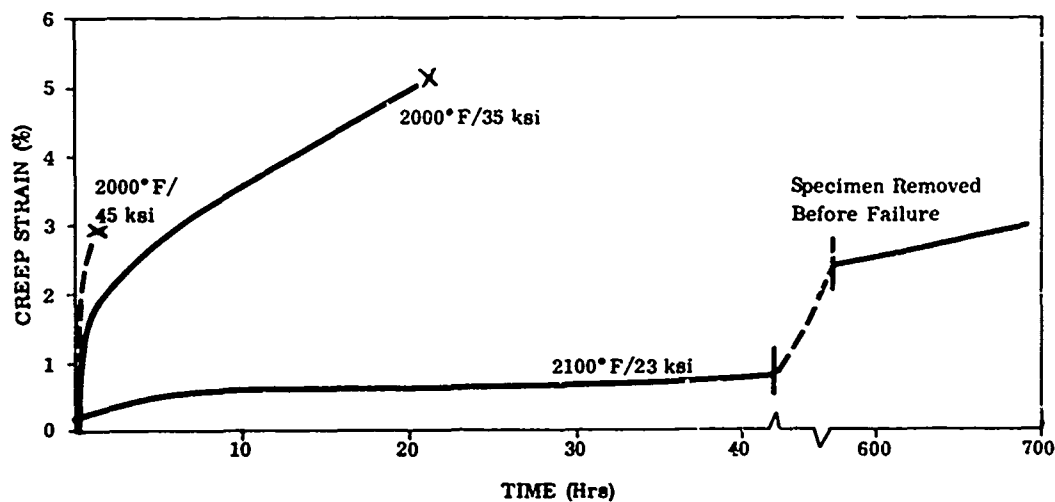SOME HIGH-STRENGTH MATERIALS

FIGURE 35. CREEP OF COATED Cb(ALLOY)/26%W IN AIR;
Specimens Show 3 Percent Creep Strain or More
Before Failure

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for Cb(Alloy)/W system was investigated by heat treating the composite specimens for various times at 2200°F and then testing the specimens in tension at the same temperature. The changes in composite strength at 2200°F induced by these pre-test heat treatments are shown in Figure 36. There is a modest decrease in longitudinal tensile strength with increasing pre-test heat-treating time but an increase in composite strength for the other orientations.
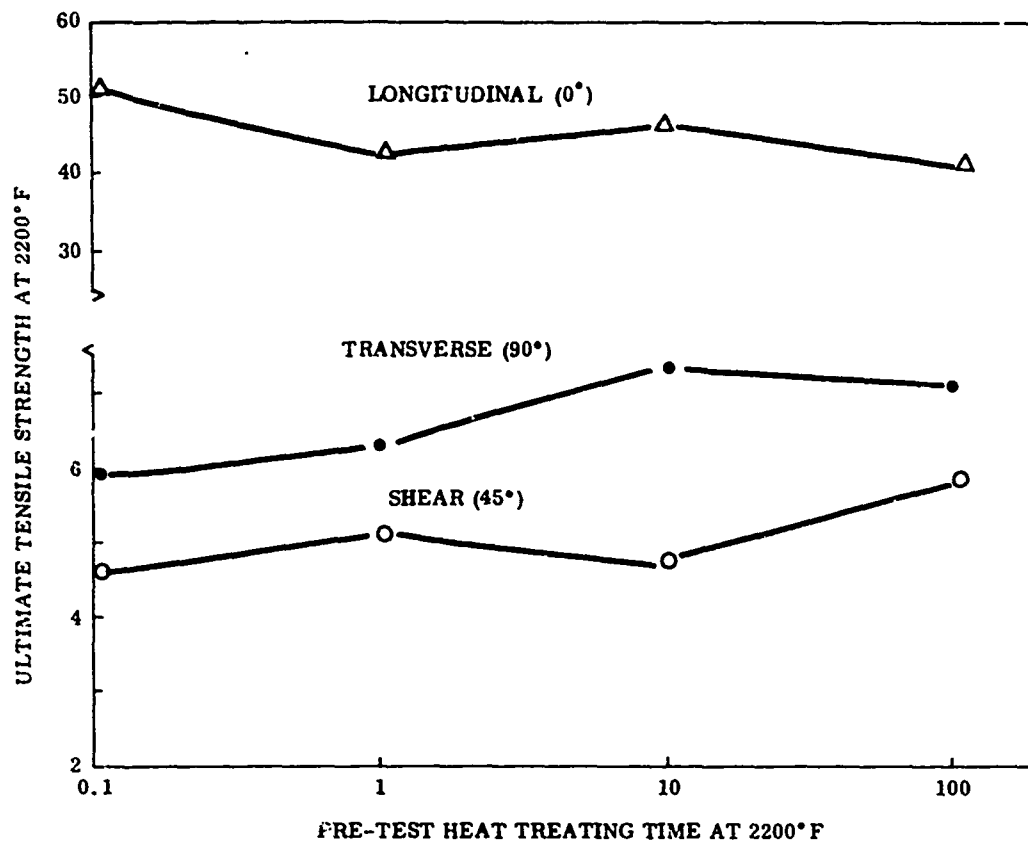

FIGURE 36. EFFECT OF PRE-TEST HEAT TREATMENTS AT 2200°F
ON STRENGTH OF Cb(ALLOY)/24W AT 2200°F FOR
DIFFERENT FILAMENT ORIENTATIONS

7.4 FAIL-SAFE PROTECTION

The fail-safe protection of the composite in event of coating damage is provided by the matrix and the relative affinity of the matrix and the filaments for oxygen. There are two functions the matrix should perform to provide maximum fail-safe life:

1. First, the matrix should be oxidation resistant so that it is consumed slowly by oxidation. This is the first fail-safe protection.

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2. Second, the matrix should have a greater affinity for oxygen than the filaments. This will prevent filament oxidation until the matrix itself is consumed or in the event of oxidation of a few filaments, oxidation of the remaining filaments will be delayed. This is the second fail-safe protection.

Figure 37 shows the oxidation rates of the two alloys used as matrices in the Cb(Alloy)/W composite and the oxidation rates of some other oxidation-resistant alloys where comparable data are available. As shown in this figure, the oxidation resistance of both Solar alloys (B-1V and J-Alloy) compare favorably with the oxidation rates of the other alloys. The B-1V alloy (Cb-42Ti-4Cr-4Al-1V) is currently used as a matrix because of its greater ductility, but the J-Alloy (Cb-40Ti-9Cr-4Al) could be used as an outer composite layer to afford greater oxidation resistance.

Figure 38 shows the oxidation rate and the time to first filament attack for an uncoated specimen and for a coated specimen with the entire coating removed. Also shown is the oxidation rate for a coated specimen (dashed line). The time for the first filament attack for these specimens is indicated by the hatched regions in this figure As will be shown later, the time for first filament attack can be considerably less than the time for composite failure because of the second fail-safe mechanism, i.e., protection of the remaining filaments by sacrificial oxidation of the matrix.

Results showing the time to first filament oxidation (first fail-safe protection) are listed in Table XXIV. The uncoated specimen and the specimen with the entire coating removed show the shortest time to first filament oxidation. Specimens with 25- and 50-mil holes in the coating have greater fail-safe lives. The latter specimens more closely approach conditions likely to be encountered when the coating is damaged in service and thus these times are closer to the first fail-safe life that will be significant in use of the composite. As shown in Figure 39, the filaments have not been attacked after a 50-hour exposure in air at 2000°F (continued tests show that this time exceeds 100 hours before first filament attack).

The second fail-safe protection of this system is illustrated in Figure 40. The specimen shown (J-Alloy matrix) was tested under load (20 ksi) in air at 2000°F after an exposed edge filament was first oxidized. The specimen did not fail in 120 hours after first filament attack because of the second fail-safe protection. Additional filaments were oxidized in this period of time, but damage was still not sufficient to cause composite failure. Final failure time is dependent upon the load, and the ratio of oxidized to unoxidized filaments. Thus, the second fail-safe life will be greater for low loads and composites with more layers of filaments.
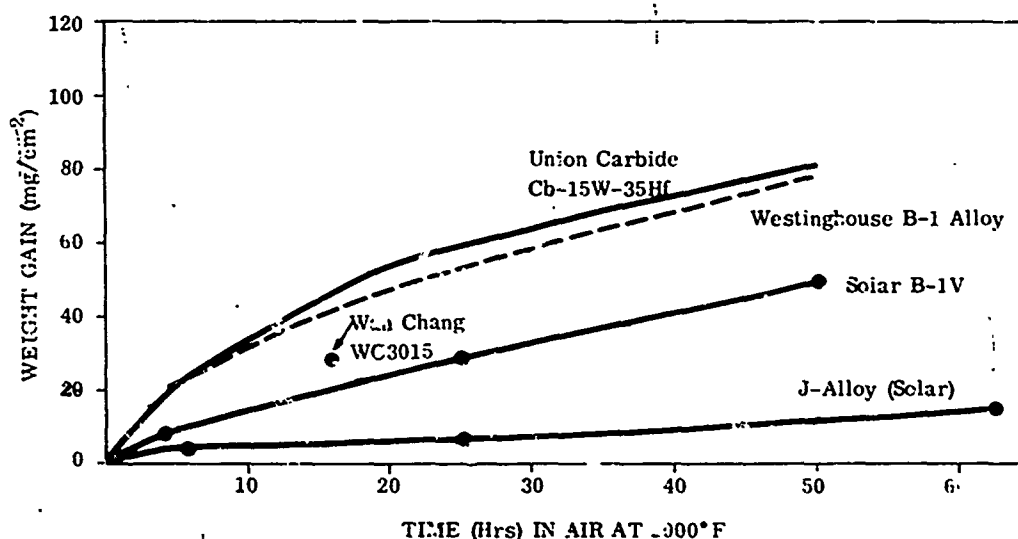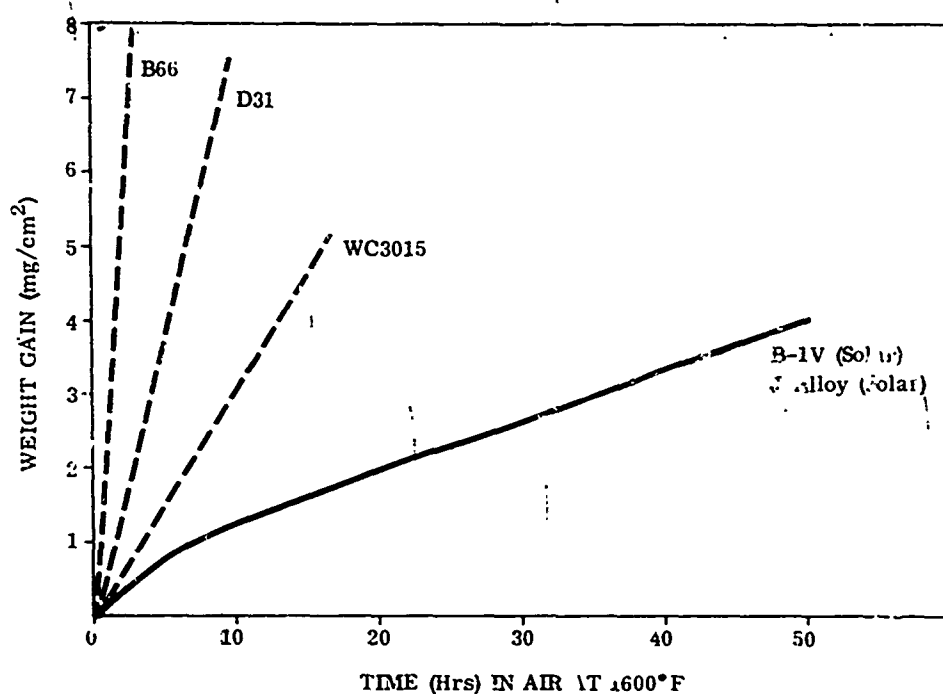
FIGURE 37. COMPARISON OF OXIDATION RATES OF SOLAR'S J AND B-1V ALLOYS USED AS COMPOSITE MATRICES WITH THE OXIDATION RATES OF OTHER OXIDATION-RESISTANT ALLOYS
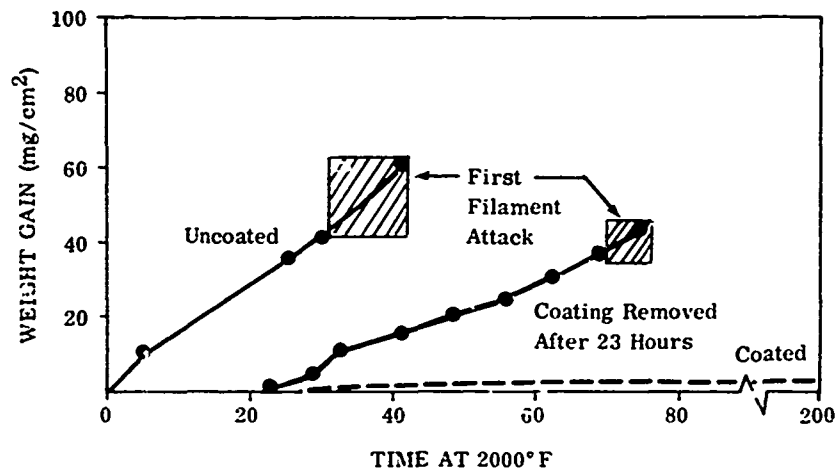
FIGURE 38. WEIGHT GAIN VERSUS OXIDATION TIME AT 2000°F FOR
Cb(ALLOY)/W; The Time to First Filament Attack is
Indicated by the Hatched Regions

TABLE XXIV

FIRST FAIL-SAFE PROTECTION OF COMPOSITE

Condition	Exposure	Time to First Filament Attack (hrs)
Uncoated	2000°F in Air	30 to 41
Silicided plus 23 Hours at 2000°F and Coating Removed	2000°F in Air	46 to 50
Silicided plus 20 Hours at 2000°F and 0.050-Inch Hole in Coating	2000°F in Air	105
Silicided plus 20 Hours at 2000°F and 0.025-Inch Hole in Coating	2000°F in Air	>100
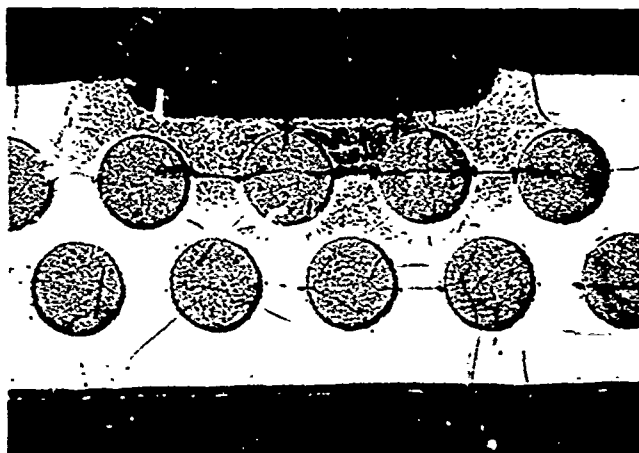
Magnification: 50X

FIGURE 39.

SECTION AT 50-MIL HOLE IN
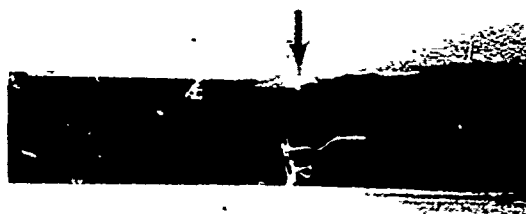COATING AFTER A 50-HOUR
EXPOSURE IN AIR AT 2000°F

FIGURE 40.

RADIOGRAPH SHOWING SECOND
FAIL-SAFE PROTECTION OF
COMPOSITE; Specimen Was Tested
in Air for 120 Hours at 2000°F Under
a 20 ksi Load After Exposed Edge
Filaments Were First Oxidized

To summarize, the first fail-safe life of this composite exceeds 100 hours for normal coating damage. The second fail-safe life is dependent upon the load but will also exceed 100 hours at 2000°F for loads yielding 20 ksi or less and for thicker composites.

7.5 CYCLIC HEAT TREATMENTS

A series of tests were performed to determine the effect of cyclic heat treatments in a simulated rig tester on the oxidation of coated composite. Coated specimens were subjected to 1-hour cycles at 2000°F. About 40 seconds were required for heating and cooling. After cycling, the specimens were sectioned and examined metallographically for coating cracks leading to matrix oxidation. It was found that the number of cycles before coating cracks opened could be increased by increasing the thickness of matrix covering the outer filament layers. This study is still underway, but the results thus far are summarized in Figure 41. The graph shows the approximate cycles to cause coating cracks versus the matrix thickness covering the filaments. As shown in this figure, a thicker matrix covering over the filaments yields a composite that can withstand a greater number of cycles before cracks appear in the coating.
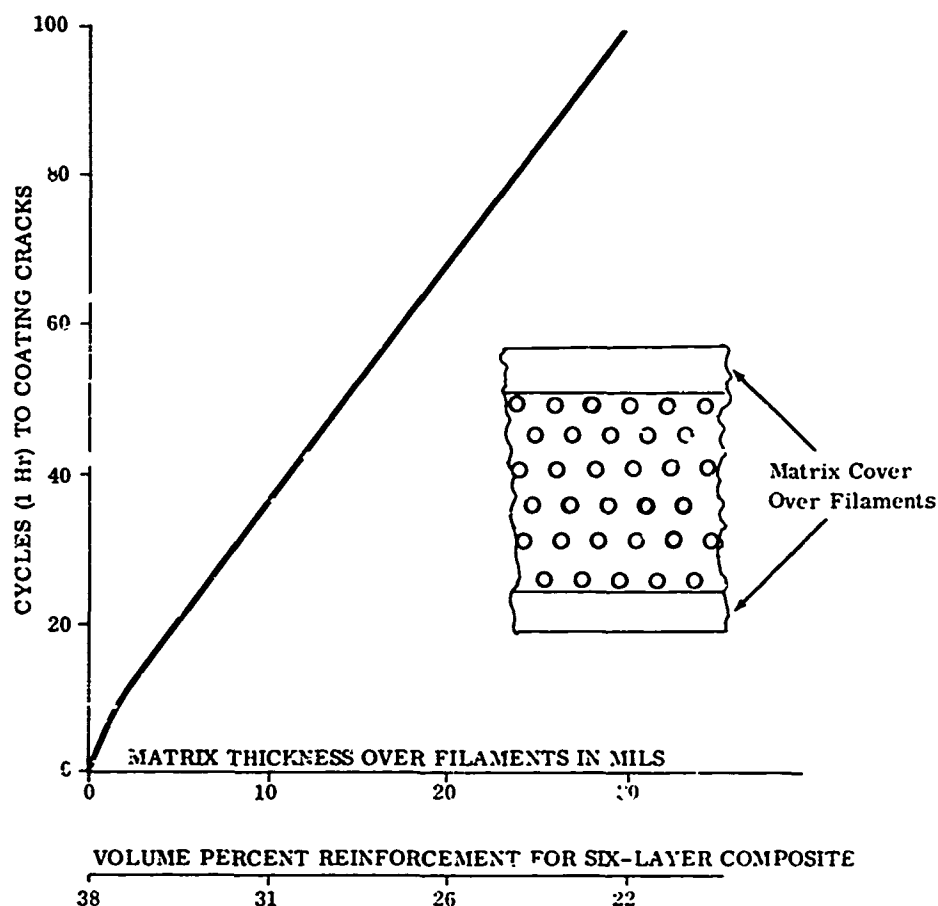
FIGURE 41. ESTIMATED MATRIX COVER OVER TUNGSTEN
FILAMENTS REQUIRED TO PREVENT CRACKS
IN COATING FOR SPECIMEN SUBJECTED TO
CYCLIC RIG TESTS: The Change in Volume
Percent Reinforcement with Matrix Cover for
Six-Layer Composite is Also Shown

The variation in volume percent with matrix cover is also shown in this
figure for a six-layer composite. For example, a 25 volume percent composite with
a matrix cover of 15 mils could withstand about 75 cycles before cracks open in the
coating. Because of the double fail-safe protection of this system, however, cracks
in the coating would not lead to composite failure until the composite had been sub-
jected to additional cycles.

7.6 FABRICABILITY AND WORKABILITY

High-quality composites are relatively easy to fabricate since both matrix and filaments are ductile and non-reactive. The matrix can be reduced from arc-melted ingots to 10-mil foil with only one intermediate heat treatment. Filament breakage is no problem as in some composite systems because the filaments are ductile. Because of this, and since the filaments and matrix are non-reactive, mechanical properties meet or exceed rule-of-mixtures values and are reproducible with a low coefficient of variation.

Although only a limited amount of composite working has been performed, the general workability of the system has been demonstrated. For example, the composite can be rolled to 85 percent reduction in thickness without any intermediate heat treatments or damage to the composite. Cross sections of the rolled composite were shown in Figure 5 (Sec. 4.1.2) and Figure 6 (Sec. 4.2.1) before and after transverse tensile testing at 2200°F. The cold rolling has not significantly affected the transverse tensile strength of the composite.

7.7 MATRIX CRACKS AND POROSITY

There are two structural features that appear in the composite after extended heat treatments which reduce the low-temperature transverse strength and ductility. These structural features are radial cracks in the matrix around the filaments and porosity at the interface. Matrix cracking near the filaments is caused by enrichment of the matrix with tungsten to such a degree that the matrix is embrittled in the region near the filaments. The porosity at the interface is caused by unequal filament-matrix diffusion.

The heat-treating conditions resulting in the formation of these structural features in the composite are listed in Table XXV. Work is still un ' way to more clearly define the effect of these heat treatments and structural features on mechanical properties.

TABLE XXV

TIME FOR FORMATION OF MATRIX CRACKS AND POROSITY IN COMPOSITE

	Time at 2000°F (hrs)	Time at 2200°F (hrs)	Time at 2400°F (hrs)
Matrix Cracks[1]	100 to 200	100 to 150	10
Porosity	> 200	100 to 150	>10

1. Determined by examination of transverse tensile specimens.

7.8 DUCTILITY

The data presented earlier show that the columbium alloy/tungsten composite has elongations at fracture that are generally in excess of 3 percent. The composite may be reduced large amounts at room temperature providing further evidence of the ductility of the material. This combination of high stress-to-rupture and ductility-at-rupture is unique. The highest strength superalloys such as MarM200 are limited to several hundred degrees lower temperature but even at these lower temperatures, they fail with limited plastic deformation (e.g., 2 to 5 percent). The directionally solidified eutectics such as Ni_3Al-Ni_3Cb are also limited in temperature and the stronger material fails at small deformations, typically 2 percent, but have the added disadvantage of a rapid decrease in strength due to instability. Attention has turned recently to ceramic-type materials such as silicon carbide and silicon nitride. These have similar strengths to Cb alloy/tungsten but their lower density gives them superior strength-to-density. However, the usefulness of this superior strength is limited by several factors. First, the consistency of the strength of a brittle material is low. A typical coefficient of variation of strength may be 10 to 20 percent as opposed to typically 1 percent for a ductile material. To remain below the 3σ (standard deviation), lower limit of strength restricts the maximum stress to 0.4 to 0.7 $\overline{S}$ where $\overline{S}$ is the average strength. Second, the design stress must be a smaller fraction than usual of the maximum stress because of the lack of ductility. Third, there is a marked size effect with brittle materials so that design stresses are further reduced. Fourth, the effect of adventitious stress concentrators is markedly more serious than with materials possessing some ductility. For example, recent work at General Electric for NASC showed that cracks of 46 microns in length were required to explain the low average room-temperature strength of silicon bonded SiC of 40,700 psi, in good agreement with the 50 micron cracks observed to be caused by diamond grinding. Similar data from Stanford Research Institute on diamond-ground alumina shows excellent agreement between calculated and observed cracks. Further, these materials are not ductile at 2000°F so that the effects are not limited to low temperatures. Also, the work at General Electric showed that annealing at 1700°C (3100°F) did not heal the cracks.

The columbium alloy/tungsten composites offer by far the best combination of strength and ductility available in any material.